FLUCTUATION THERMODYNAMIC PROPERTIES OF NONELECTROLYTE LIQUID MIXTURES

BY

ROBERT JOSEPH WOOLEY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1987

to Sue, for her patience and

encouragement.

ACKNOWLEDGEMENTS

I would like to thank Dr. J. P. O'Connell for his help and guidance throughout this study. Further, I wish to thank Dr. Robley C. Williams, Jr., of Vanderbilt University for his enthusiastic help and many thoughtful suggestions on how to install a laser on an old ultracentrifuge. His sincere interest in a project not actually in his field was inspiring.

I also wish to thank Dr. Fricke who had his differential refractometer fixed so that I could use it and Dr. Mike Young and his lab workers for tolerating my presence and allowing me unlimited free use of their microcomparator for many long hours of measurements.

I am grateful to Stewart Goldfarb for making his Dortmund VLE database available to me and to the Valdosta State College Library who allowed me to check out VLE data books that were not available anywhere in the State of Florida.

I would also like to thank Sue Wooley for her assistance in typing, proofreading and formatting this final document.

TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS iii

KEY TO SYMBOLS vii

ABSTRACT xii

CHAPTERS

1 INTRODUCTION 1

2 DETERMINATION OF SOLUTION THERMODYNAMIC PROPERTIES BY RAYLEIGH LIGHT SCATTERING 6

Introduction 6
Background 7
Rigorous Thermodynamic Fluctuation Development 11
Light Scattering in Relaxing Solutions 15
Calculation of Thermodynamic Properties 18
  Fluctuation Properties 18
  Activity Coefficients 18
  Activity Coefficients from Equation (2-46) 19
  Comparisons with Phase Equilibrium Measurements .. 23
Sensitivity of Activity Coefficient Calculations 25
Summary 30

3 CONCENTRATION DERIVATIVES OF DILUTE SOLUTION ACTIVITY COEFFICIENTS USING AN ANALYTICAL ULTRACENTRIFUGE 32

Introduction 32
Equipment 40
  Apparatus 40
  Composition Detection 41
System Selection 45
Error Analysis 49
Summary 52

4 EXPERIMENTAL MEASUREMENTS OF DILUTE SOLUTION ACTIVITY COEFFIEIENT DERIVATIVES 53

Introduction 53
Carbon Disulfide/Acetone System 54
Chloroform/Acetone System 60
Carbon Tetrachloride/Acetone System 64
Benzene/Acetonitrile System 68
Carbon Tetrachloride/Methanol System 72
Summary of Experimental Results 76
Pressure Effects on the Results 77
The Effect of Imputities on Ultracentrifugation 81
Summary 82

5 DIRECT CORRELATION FUNCTION INTEGRAL DATABASE AND MODELING 83

Introduction 83
DCFI Database 87
  Isothermal Compressibility Data 91
Thermodynamic Property Modeling 99
  DCFI Modeling 99
  Activity Coefficient Modeling from DCFIs 100
Summary 115

6 SUMMARY 119

APPENDICIES

A ULTRACENTRIFUGE OPERATION 124

B LASER LIGHT SOURCE FOR MODEL E ULTRACENTRIFUGE INSTALLATION AND ALIGNMENT 138

C FORTRAN PROGRAM FOR CONVERSION OF FRINGE MEASUREMENTS TO COMPOSITION PROFILES IN THE ULTRACENTRIFUGE FRNGCNV AND FRNGCNVP 149

D EXCESS VOLUME AND PARTIAL MOLAR VOLUME CALCULATIONS 165

E CALCULATION OF INITIAL ULTRACENTRIFUGE SPEED 167

F RESULTS OF EXPERIMENTAL ULTRACENTRIFUGE MEASUREMENTS OF FIVE BINARY SYSTEMS 169

G FORTRAN PROGRAMS FOR THE CALCULATION FOR PVT CALCULATIONS AND DATA REGRESSION 228

H DIRECT CORRELATION FUNCTION INTEGRAL DATABASE 247

I FORTRAN PROGRAMS FOR REGRESSION OF ACTIVITY COEFFICIENT DATA TO EQUATIONS 5-39a AND 5-39b 306

BIBLIOGRAPHY 311

BIOGRAPHICAL SKETCH 319

KEY TO SYMBOLS

A	Composition profile in ultracentrifuge uncertainty analysis.
$A(k)$	Relaxation correction to $J(k)$.
A_{12}	Margules Binary Parameter.
A_{21}	Margules Binary Parameter.
$B(k)$	Relaxation correction to $J(k)$.
B_{ij}	Matrix Element, Eq. 2-18.
B_k	Characteristic parameter, Eq. 2-26.
C_P	Heat capacity at constant P.
C_V	Heat capacity at constant V.
C_{11}	Direct Correlation Function Integral between two type 1 compounds.
C_{12}	Direct Correlation Function Integral between a type 1 and a type 2 compound.
C_{22}	Direct Correlation Function Integral between two type 2 compounds.
C^*	Characteristic parameter, Eq. 5-19.
C^*_M	Characteristic parameter of a mixture, Eq. 5-19.
C_k	Characteristic parameter, Eq. 2-26.
ΔC	Grouping of direct correlation function integrals.
D	Activity coefficient derivative in ultracentrifuge uncertainty analysis.
$\mathcal{D}$	Diffusion coefficient.
F	Factor in Eq. 2-48.

G_{12}	NRTL binary parameter.
G_{21}	NRTL binary parameter.
J	Ratio of Rayleigh peak to the Brillouin peak.
$J(0)$	J corrected to 0 wave vector.
$J(k)$	J as measured.
J_{ID}	J ideal.
K	Grouping of variables, Eq. 2-44b.
M_1	Molecular weight, component 1.
N_R	Random number.
P	Pressure.
R	Gas constant.
R_{90}	Rayleigh ratio measured at 90°.
R_C	Composition contribution to Rayleigh Ratio.
$R_{C,D}$	Composition and density cross contribution to Rayleigh Ratio.
R_D	Density contribution to Rayleigh Ratio.
R_{IS}	Isotropic portion of Rayleigh ratio.
ΔS_T	Total entropy change.
S	Entropy.
T	Temperature.
T^*	Characteristic parameter, Eq. 5-19.
T^*_M	Characteristic parameter of a mixture, Eq. 5-19.
U_i	Uncertainty of variable i.
V	Volume.
$\overline{V}_i$	Partial molar volume of component i.
a	Binary parameter, Eq. 5-39.

a_i	Typical variables in uncertainty analysis.
b	Binary parameter, Eq. 5-39.
c	Speed of light.
c_{ij}	Direct correlation function.
d	Approach to equilibrium.
f	Parameter in Eq. 2-33.
g_{ij}	Radial distribution function.
h_{ij}	Total correlation function.
$\overline{h}^E$	Excess enthalpy.
i_C	Intensity of Rayleigh peak.
i_B	Intensity of Brillouin peak.
j	Fringe number.
Δj_P	Change in fringe number due to pressure.
k	Boltzman constant.
k_V	Wave vector.
k	Compression.
n	Refractive Index.
Δn_P	Refractive Index change due to pressure.
r	Parameter in Eq. 2-43, Chapter 2.
r	Radius from center of Rotor, Chapter 3.
t_δ	Time to Equilibrium.
v_∞	Infinite frequency velocity of sound.
v_o	Zero frequency velocity of sound.
v^E	Excess Volume.
v_S	Velocity of sound.

w	Width of centrifuge cell.
x_i	Mole fraction, component i.
$x^{(1)}$	Parameter in Eq. 2-6.
$y^{(1)}$	Parameter in Eq. 2-5.
$y^{(2)}$	Parameter in Eq. 2-9.
α_P	Coefficient of thermal expansion.
Δ_i	Portion of scattered light transferred from side peak to the central peak.
δ	Approach to equilibrium.
ϵ	Dielectric constant.
γ_i	Activity coefficient of component i.
γ_C	C_P / C_V.
γ^{∞}	Infinite dilution activity coefficient.
κ_S	Adiabatic compressibility.
κ_T	Isothermal compressibility
κ_T^E	Excess isothermal compressibility.
λ or λ_o	Wave length of incident light.
μ_i	Chemical potential of component i.
$\Delta\upsilon$	Frequency of peak separation.
υ	Frequency of incident light.
ρ	Density.
ρ_i	Concentration of component i.
ρ_u	Depolarization ratio.
ρ^*	Characteristic parameter, Eq. 5-19.
ρ_M^*	Characteristic parameter of a mixture, Eq. 5-19.

τ_{12}	NRTL parameter.
τ_{21}	NRTL parameter.
τ	Relaxation time.
θ	Scattering angle.
ω	Rotational speed.
ν	Volume of centrifuge cell.
χ	Reduced bulk modulus.
$\langle(\Delta\epsilon)^2\rangle$	Total mean square fluctuation in dielectric constant.
$\langle(\Delta\epsilon)^2_C\rangle$	Central peak contribution to the dielectric fluctuation.
$\langle(\Delta\epsilon)^2_{ADIAB}\rangle$	Adiabatic contribution to the dielectric fluctuation.
$\langle(\Delta\rho)^2\rangle$	Mean square density fluctuation.
$\langle(\Delta x_2)^2\rangle$	Mean square composition fluctuation.

Superscripts

^{o}	Pure component property, or initial concentration.
^{ID}	Ideal property.
^{E}	Excess property.

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

FLUCTUATION THERMODYNAMIC PROPERTIES OF NONELECTROLYTE LIQUID MIXTURES

By

Robert Joseph Wooley

December 1987

Chairman: John P. O'Connell
Major Department: Chemical Engineering

The behavior of the concentration derivatives of the pressure and component activity coefficients has been studied via their connection to integrals of the statistical mechanical direct correlation function (DCFI). Consideration of their direct experimental accessibility with light scattering and equilibrium sedimentation in an ultracentrifuge was made and dilute solution data have been taken with the latter method. A new binary solution model, based on simplified forms of the DCFI and reduced bulk modulus, has achieved good agreement with a newly compiled database of DCFI and fluctuation properties for nonelectrolytes.

The data needed to establish a new theory based on fluctuation solution properties do not include reliable values of activity coefficient derivatives at low concentrations. These are usually obtained by differentiation of a specific model with parameters fitted to vapor-liquid equilibrium data with results greatly affected by the model chosen. As alternatives, two experimental methods for direct determination of the activity coefficient derivative have been explored.

It has been concluded that measurement of concentration fluctuations of binary systems with light scattering techniques is not useful for activity coefficients because of sensitivity to experimental error and excessive requirements of ancillary data.

Equilibrium sedimentation in an analytical ultracentrifuge has been judged more promising and measurements have been made with a Beckman Model E apparatus with a newly installed laser optical system for Rayleigh fringe detection. Measurements have been made of five systems that meet well-defined criteria for refractive index and density differences as well as solution nonideality.

The measured chemical potential derivatives have been found to be lower than those calculated from VLE models. However, in each system a single multiplicative factor generally brings the results to within experimental error of the VLE models. These values support the low concentration extrapolations of the Wilson and NRTL Equations. It was not possible to distinguish the better of these models for activity coefficient derivatives.

A database of DCFI values for 28 strongly nonideal binary systems has been assembled using liquid compression and excess volume data along with Wilson and NRTL parameters fitted to VLE data. Modeling of the DCFIs and activity coefficients was attempted. While the density dependence is extremely complex, a successful approach for activity coefficients is to separate the activity coefficient derivative into a function of DCFIs, $1/\Delta C$, and the reduced bulk modulus, χ. The results are generally insensitive to the mathematical form chosen for $1/\Delta C$ so a linear expression has been used along with an idealized variation of χ to obtain a new binary activity coefficient model. Least squares fits to all systems in the database yielded excellent results.

CHAPTER 1

INTRODUCTION

With continually increasing energy, raw material, and capital costs, chemical process design engineers are constantly called upon to lower the costs associated with the design and operation of chemical plants. Recent advances in computer simulation technology allow the process engineer to rapidly assess the feasibility and economics of new processes and process modifications, thus helping reduce capital and operating costs with more optimum designs. However, while these computer simulators can easily describe unit operations and converge flowsheets with complex recycles, they are limited by their ability to model and predict the physical properties needed for a reliable design. Further, physical property calculations, especially phase equilibria properties, usually consume a considerable amount of the computer time in process simulation (O'Connell, 1983). Finally, most empirical models for phase equilibrium calculations can require exhaustive amounts of binary and sometimes multicomponent data, especially if the compounds are highly non-ideal or unusual. As a result, new and different processes, such as those found in synthetic fuels and bioprocessing, continue to tax the currently available models. The consequence of all of this is that computer simulation requires simple and reliable models for process design of current and future systems.

To meet this demand, new thermodynamic property models, free of common simplifying assumptions, such as pairwise additivity of intermolecular forces, rigid molecules, etc. are needed. The fluctuation solution approach (Kirkwood and Buff, 1951; O'Connell, 1971; 1981) offers these advantages. Kirkwood and Buff (1951) formulated the density derivatives of the chemical potential and total system pressure in terms of integrals of the radial distribution function. O'Connell (1971) used these formulations and the Ornstein and Zernike (1914) equations to give the thermodynamic properties in terms of the direct correlation function integrals (DCFI). These direct correlation functions appear relatively insensitive to the details of intermolecular interactions and may be modeled with simple functions. Additionally, because the thermodynamic properties are obtained by integration, the results can be much less sensitive to their parameterization. For example, Mathias and O'Connell (1979, 1981) found that this approach worked very well for gases dissolved in liquids.

With models for the direct correlation function integrals, the solution density and the chemical potential, essential in phase equilibrium calculations, can be calculated or predicted from the pressure, temperature and composition. In particular, such a model may allow for accurate modeling of the activity coefficient of highly non-ideal systems.

The DCFIs modeled by Mathias and O'Connell (1979, 1981) work well for liquids containing supercritical components (dissolved gases) but apparently not as well for condensed-phase systems (Campanella, 1984). Campanella made an attempt to model the DCFI for vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) systems in a fashion similar to that of Mathias (1978), using a hard sphere term and a perturbation term. He found in VLE systems that the hard sphere term did not show adequate compositional variation. Further, at low concentrations the data used to calculate DCFIs were not accurate enough to properly determine the compositional dependence in that region. His work was hindered by having to calculate activity coefficient derivatives indirectly by differentiating either tabulated phase equilibria data or data from a model, such as Wilson (1964). This has lead to uncertainty in the actual compositional behavior of DCFIs.

The objective of the present work has been to explore the compositional behavior of the DCFI in more detail. The relationships between DCFIs and mole fractions and measurable binary quantities of isothermal compressibility, κ_T, partial molar volume, $\overline{V}_i$, volume, V, and activity coefficient derivatives, $\left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{T,P}$ lead to DCFI values from experiment. Binary data have been collected (aided by the recent compilation of isothermal compressibilities by Huang (1986)) on non-ideal systems and a database of DCFIs for a wide variety of systems has been created.

A problem in developing an accurate DCFI database is the collection of accurate activity coefficient derivative data. Typically, this quantity would be calculated by differentiating a specific activity coefficient model whose parameters are fitted to vapor-liquid equilibrium data. However, as Campanella (1984) has pointed out, there can be a significant difference in the activity coefficient derivative depending on the model chosen to fit the VLE data. This effect is especially apparent in the low concentration regions where the various activity coefficient models can give significantly different values. Also, extrapolations of finite concentration VLE data do not necessarily agree with directly measured infinite dilution activity coefficients (Loblen and Prausnitz, 1982; Schreiber and Eckert, 1971), suggesting further uncertainity in reliability of the activity coefficient models fitted to VLE data in this region.

To eliminate the need for an intervening activity coefficient model between experimental VLE data and the activity coefficient derivative, methods have been explored for experimental measurements that directly yield the activity coefficient derivative, especially in dilute regions. In addition to its use in DCFI model development, such data could be used by others in establishing new activity coefficient models.

Two methods for determining the activity coefficient derivatives directly have been considered. The potential use of Rayleigh light scattering is explored in Chapter 2. Several authors (Coumou and Makor, 1964; Brown et al., 1978; Miller, 1967; Miller and Lee, 1973; Maguire et al., 1981) have described procedures for finding thermodynamic properties from light scattering. These involve measuring the contribution of concentration fluctuations to the light scattering either with the ratio of the total light scattered at an angle of 90° to the incident light or the ratio of the scattered central Rayleigh peak to Brillouin side peaks. This leads to several different methods for connecting light scattering measurements to thermodynamic properties, many involving approximations that are subject to question. Therefore, a thorough analysis of the procedure and errors involved in obtaining activity coefficients using light scattering data has been performed. The method requires a considerable amount of auxiliary data and appears to be limited in its accuracy while requiring a very high refractive index difference for the chemicals being measured.

The second method considered for measuring activity coefficient derivatives is by ultracentrifugation as described in Chapters 3 and 4. This procedure has been used previously to measure activity coefficients (Cullinan and Lenczyk, 1969; Rau, 1975; Johnson et al., 1959). The composition profile established during centrifugation readily leads to the activity coefficient derivative. Chapter 3 describes the theoretical basis and expected errors involved in determining activity coefficients from ultracentrifugation. The method has the advantage over light scattering techniques of only needing mixture refractive index and density data to support the centrifuge measurements. It does require that the binary pair have a suitable difference in density, but the refractive index difference need not be extremely high.

Chapter 4 describes the experimental measurements that have been made on five systems: carbon disulfide in acetone, chloroform in acetone, carbon tetrachloride in acetone, carbon tetrachloride in methanol and benzene in acetonitrile. Ultracentrifuge measurements have been made in the 1.5% to 10% (mole) range at temperatures from 10° C to 35° C. In support of those experiments, mixture refractive index measurements have been taken in a differential refractometer on all systems. Chemical potential derivatives and activity coefficient derivatives from these measurements have been compared with vapor-liquid equilibrium data fit to the Wilson (1964) and NRTL (Renon and Prausnitz, 1968) models.

Once activity coefficient derivatives have been obtained, a database of DCFIs can be developed. As described in Chapter 5 sixteen non-ideal systems selected by Campanella (1984) for study plus twelve other non-ideal systems have been examined. For each of these systems, excess volume data, pure component compressibility data and vapor-liquid equilibrium data were known. For nineteen of the systems, mixture compressibility data are also available.

The DCFI can be conveniently divided into volumetric and activity coefficient derivative terms. To calculate an "ideal" DCFI, an ideal mixing rule is assumed for the volume and isothermal compressibility while the activity coefficient derivative term is set to zero. By subtracting this ideal DCFI from the real DCFI, determined from experimental quantities, an excess quantity, resembling the activity coefficient derivative term, remains. Models for this excess DCFI can lead to the compositional variation of these theoretically based quantities as well as aid in future modeling efforts. Campanella (1984) pointed out that most of the activity coefficient models have a common form when written in terms of the composition derivative. Chapter 5 explores the possibilities of modeling the excess DCFI with empirical forms.

The constant pressure activity coefficient derivative of a binary solution can be written in terms of the three pairwise DCFIs. This grouping of DCFIs has suggested a new empirical relationship for activity coefficients and excess Gibbs energies.

CHAPTER 2

DETERMINATION OF SOLUTION THERMODYNAMIC PROPERTIES BY RAYLEIGH LIGHT SCATTERING

Introduction

The scattering of light by a fluid medium is caused by the electric field associated with the light inducing periodic oscillations of the electrons in the sample. This leads to energy being reradiated as light, scattered at different frequencies and angles relative to the incident (Oster, 1948). By observing this scattered light as a function of the scattering angle, information about the sample can be deduced. In particular, a contribution to the light scattering by solutions is due to concentration fluctuations which can be related to the concentration derivative of the chemical potential or, equivalently, the activity coefficient (Miller, 1967). The major advantage of such an analysis is that the material is not affected by the experiment and only very small amounts of the sample are required.

Such measurements are attractive as an aid for the development of models for solution behavior. In fluctuation solution theory (Kirkwood and Buff, 1951; O'Connell, 1971; 1981) the concentration derivative of the chemical potential, along with the isothermal compressibility, and the partial molar volume are the properties needed to determine the three pair-correlation function integrals of a binary solution. While there are often sufficient data from vapor pressure measurements to accurately calculate the composition derivative of the chemical potential at midrange concentrations of the components, the accuracy deteriorates at low concentrations. To develop a solution model based on correlation function integrals, non-traditional means of getting this derivative must be considered. An attractive candidate appears to be light scattering, since it leads directly to the derivative.

Previous work in this area has focused on using the technique to obtain excess Gibbs energies by double integration of the concentration derivative obtained from the scattering (Brown et al., 1978; Maguire et al., 1981). The conclusion was that phase-equilibrium measurements were easier and more accurate for giving this quantity. In particular Miller and Lee (1973) pointed out that a refractive index difference of at least 0.2 between the pure components is required in a system to produce reliable results by light scattering. If that is truly the case, most common organic systems of interest would be eliminated.

Several different analyses connecting the light-scattering measurements to the desired quantities have appeared (Brown et al., 1978; Maguire et al., 1981; Coumou and Mackor, 1964; Miller, 1967; Miller and Lee, 1973), many involving approximations that are subject to question. To quantitatively test whether the method can be used, the system cyclohexane/benzene, a typical system of lower refractive index difference ($\Delta n = 0.07$) for which all of the auxiliary properties are available, was examined here.

This chapter describes the basis and procedures necessary to obtain information on excess Gibbs energies, activity coefficients and their derivatives. Included is a sensitivity analysis to decide on the method's utility as well as delineation of all the thermodynamic property information required for the technique.

Background

When light is scattered from a solution, there exists a central, unshifted peak of highest intensity, known as the Rayleigh peak, and two shifted (Brillouin) peaks of lesser intensity on either side. The concentration fluctuations contribute only to the central Rayleigh peak (Miller, 1967). Einstein (1908) originally developed the Rayleigh Ratio, the ratio of the intensity of the Rayleigh Peak to that of the incident light. From Einstein's theory, the Rayleigh Ratio measured at a scattering angle of 90° can be written as a function of the mean squared fluctuation of the dielectric constant, ϵ.

$$R_{IS} = \frac{\pi^2}{2\lambda^4} \; V\langle(\Delta\epsilon)^2\rangle \qquad (2\text{-}1$$

where R_{IS} is the measurable isotropic portion of the Rayleigh Ratio at 90°. If the scattered light is not all depolarized, the isotropic portion must be extracted from the total scattering with the appropriate Cabannes (1929) factor.

$$R_{IS} = R_{90} \left(\frac{6 - 7\,\rho_u}{6 + 6\,\rho_u} \right) \qquad (2\text{-}2$$

where ρ_u is the depolarization ratio. For pure components $\langle(\Delta\epsilon)^2\rangle$ was originally approximated as a function of density only.

$$\langle(\Delta\epsilon)^2\rangle = \left(\frac{d\epsilon}{d\rho} \right)^2 \langle(\Delta\rho)^2\rangle \qquad (2\text{-}3$$

Coumou et al. (1964) pointed out that another thermodynamic variable (temperature or pressure) would be required to describe this fluctuation properly. To determine which of these variables would be most appropriate, they wrote $\langle(\Delta\epsilon)^2\rangle$ as a function of density and temperature as well as of density and pressure. The fluctuation in ϵ as a function of temperature and density is

$$V\langle(\Delta\epsilon)^2\rangle = \frac{kT}{\kappa_T} \left(\frac{\partial\epsilon}{\partial P} \right)_T^2 [1 + y^{(1)}] \qquad (2\text{-}4$$

where

$$y^{(1)} = \left[\frac{\kappa_T}{\kappa_S} - 1 \right] [x^{(1)}]^2 \qquad (2\text{-}5$$

$$x^{(1)} = 1 + \frac{\kappa_T}{\alpha_P}\left(\frac{\partial\epsilon}{\partial T}\right)_P \Big/ \left(\frac{\partial\epsilon}{\partial P}\right)_T = 1 + \frac{\kappa_T}{\alpha_P}\left(\frac{\partial n}{\partial T}\right)_P \Big/ \left(\frac{\partial n}{\partial P}\right)_T \qquad \text{(2-6}$$

with κ_T and κ_S are the isothermal and adiabatic compressibilities, respectively, and n is the refractive index. This treatment assumes that

$$\rho\left(\frac{d\epsilon}{d\rho}\right) \approx \frac{1}{\kappa_T}\left(\frac{\partial\epsilon}{\partial P}\right)_T = \frac{2n}{\kappa_T}\left(\frac{\partial n}{\partial P}\right)_T \qquad \text{(2-7}$$

It is also possible to write $\langle(\Delta\epsilon)^2\rangle$ as a function of density and pressure

$$V\langle(\Delta\epsilon)^2\rangle = \frac{kT\kappa_T}{\alpha_P^2}\left(\frac{\partial\epsilon}{\partial T}\right)_P^2 [1 + y^{(2)}] \qquad \text{(2-8}$$

where

$$y^{(2)} = \frac{2x^{(1)}}{1 - x^{(1)}} + \left[\frac{\kappa_T}{\kappa_S}[x^{(1)}]^2 \Big/ [1 - x^{(1)}]^2\right] \qquad \text{(2-9}$$

and the approximation

$$\rho\left(\frac{d\epsilon}{\partial\rho}\right) \approx -\frac{1}{\alpha_P}\left(\frac{\partial\epsilon}{\partial T}\right)_P = -\frac{2n}{\alpha_P}\left(\frac{\partial n}{\partial T}\right)_P \qquad \text{(2-10}$$

has been used. With data for the partial derivatives of refractive index and compressibilities, Coumou et al. (1964) evaluated values of $y^{(1)}$ and $y^{(2)}$ and compared them to $V\langle(\Delta\epsilon)^2\rangle$ for representative substances. They found that $y^{(2)}$ was 2% to 10% of $V\langle(\Delta\epsilon)^2\rangle$, whereas $y^{(1)}$ was 0.01% to 0.1%. Therefore, the fluctuations of pure component dielectric constants are best described as a function of density and temperature because the corrections can be ignored. Combining equations (2-4) and (2-1), neglecting $y^{(1)}$ and changing variables ($d\epsilon = 2n\ dn$) gives an expression for scattering by a pure component:

$$R_{IS} = R_D = \frac{2\pi^2 kTn^2}{\lambda^4 \kappa_T}\left(\frac{\partial n}{\partial P}\right)_T^2 \tag{2-11}$$

For solutions, Coumou and Mackor (1964) described the isotropic Rayleigh scattering as a function of density and concentration.

$$R_{IS} = R_D + R_C \tag{2-12}$$

Kirkwood and Goldberg (1950) gave the concentration contribution as

$$R_C = \frac{2\pi^2 kT}{\lambda^4} V\, x_1 \left(n\frac{\partial n}{\partial x_2}\right)^2 \Big/ \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} \tag{2-13}$$

However, Brown et al. (1978) concluded that a cross term, $R_{C,D}$, is required to represent the interaction of the density and the concentration effects. Such a term had previously been written by Dezelic (1973),

$$R_{C,D} = \frac{\pi^2 kT\kappa_T x_1 x_2}{2\lambda^4}\left(\rho\frac{\partial \epsilon}{\partial \rho}\right)_T\left(\frac{\partial \epsilon}{\partial x_2}\right)_{T,P} \tag{2-14}$$

Using the same logic as Coumou et al. (1964), the density derivative of the dielectric constant can be replaced with the pressure derivative of the refractive index, yielding

$$R_{C,D} = \frac{2\pi^2 kTx_1x_2n^2}{\lambda^4}\left(\frac{\partial n}{\partial P}\right)_T\left(\frac{\partial n}{\partial x_2}\right)_{T,P} \tag{2-15}$$

Thus the full connection of experiment to chemical potential derivative can be made from equations (2-11), (2-13), (2-15) and (2-16).

$$R_{IS} = R_D + R_C + R_{C,D} \tag{2-16}$$

The value for R_C yields the desired concentration derivative.

While the added cross term of Brown et al. (1978) improved results over the earlier work of Coumou and Mackor (1964) for some systems, their general contention was that the method was not as accurate as standard phase equilibrium methods for activity coefficient determination. This is true because of the many ancillary measurements that must be made along with the light scattering intensity to determine the activity coefficient. These other properties include

R_{90},	the Rayleigh Ratio at scattering angle of 90°,
ρ_u,	the depolarization ratio, calculated from polarizabilities,
ρ,	the solution density,
κ_T,	the isothermal compressibility,
n,	the refractive index,
$\left(\frac{\partial n}{\partial x_2}\right)_P$,	the composition derivative of the refractive index,
$\left(\frac{\partial n}{\partial P}\right)_T$,	the pressure derivative of the refractive index.

Equation (2-16) gives a relationship between light scattering measurements and thermodynamic properties which uses approximations in the form of the cross-term and of the density derivative of the refractive index. A parallel, but more general development has also been done.

Rigorous Thermodynamic Fluctuation Development

The rigorous treatment purposely by-passes the density and concentration crossterms (Miller, 1967). Instead, fluctuations in total entropy from variations in the temperature, volume, entropy, pressure, chemical potential of the solute and the number of moles of the solute are considered (Landau and Liftshitz, 1980).

$$\Delta S_T = \frac{-1}{2T}\ (\Delta T \Delta S - \Delta P \Delta V + \Delta\mu_2 \Delta\rho_2) \qquad (2\text{-}17$$

This fluctuation in total entropy can be written as a general function of any three of the state variables listed above,

$$\Delta S_T = -\frac{1}{2}\sum_{i=1}^{3}\sum_{i=1}^{3} B_{ij}\, x_i\, x_j$$ (2-18

where

$$\langle x_i\, x_j\rangle = k\, B_{ij}^{-1}$$ (2-19

Choosing the three independent variables as T, P, and $\rho_2 = x_2\,\rho$, gives the others as

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_{P,\rho_2}\Delta T + \left(\frac{\partial S}{\partial P}\right)_{T,\rho_2}\Delta P + \left(\frac{\partial S}{\partial \rho_2}\right)_{P,T}\Delta\rho_2$$ (2-20

$$\Delta V = \left(\frac{\partial V}{\partial T}\right)_{P,\rho_2}\Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,\rho_2}\Delta P + \left(\frac{\partial V}{\partial \rho_2}\right)_{P,T}\Delta\rho_2$$ (2-21

$$\Delta \mu_2 = \left(\frac{\partial \mu_2}{\partial T}\right)_{P,\rho_2}\Delta T + \left(\frac{\partial \mu_2}{\partial P}\right)_{T,\rho_2}\Delta P + \left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{P,T}\Delta\rho_2$$ (2-22

By inserting equations (2-20)-(2-22) into equation (2-17) and using elementary thermodynamics, we find

$$\Delta S_T = -\frac{1}{2}\left[\frac{C_P}{T^2}\,(\Delta T)^2 - \frac{2V\alpha_P}{T}\Delta T\Delta P + \frac{V\kappa_T}{T}\,(\Delta P)^2 + \frac{1}{T}\left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{P,T}(\Delta\rho_2)^2\right]$$ (2-23

Using equations (2-18) and (2-23), the following fluctuations can be identified,

$$\langle(\Delta T)^2\rangle = \frac{kT^2}{C_V}$$ (2-24a

$$\langle\Delta T\Delta P\rangle = \frac{kT^2\alpha_P}{\kappa_T C_V}$$ (2-24b

$$\langle(\Delta P)^2\rangle = \frac{k\,T}{V\kappa_S}$$ (2-24c

$$\langle(\Delta\rho_2)^2\rangle = k\ T \Big/ \left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T,P} \qquad \text{(2-24d}$$

$$\langle\Delta T\Delta\rho_2\rangle = \langle\Delta P\Delta\rho_2\rangle = 0 \qquad \text{(2-24e}$$

The same connection between this fluctuation theory and light scattering can be made through equations (2-1) and (2-2).

It is known that adiabatic pressure fluctuations do not mix with entropy and composition fluctuations; they contribute only to the Brillouin peaks. These are given by

$$\langle(\Delta\epsilon)^2_{\mathrm{ADIAB}}\rangle = \left(\frac{\partial\epsilon}{\partial P}\right)^2_{S,\rho_2}\langle(\Delta P)^2\rangle \qquad \text{(2-25}$$

Substituting

$$\left(\frac{\partial\epsilon}{\partial P}\right)_{S,\rho_2} = \left(\frac{\partial\epsilon}{\partial T}\right)_{P,\rho_2}\frac{TV\alpha_P}{C_P} + \left(\frac{\partial\epsilon}{\partial P}\right)_{T,\rho_2} \qquad \text{(2-26}$$

results in

$$\langle(\Delta\epsilon)^2_{\mathrm{ADIAB}}\rangle = \frac{kT^2}{C_V}\left(1 - \frac{1}{\gamma_C}\right)\left(\frac{\partial\epsilon}{\partial T}\right)^2_{P,\rho_2}$$

$$+\frac{2kT^2\alpha_P}{\kappa_T C_V}\left(\frac{\partial\epsilon}{\partial T}\right)_{P,\rho_2}\left(\frac{\partial\epsilon}{\partial P}\right)_{T,\rho_2} + \frac{kT}{\kappa_S V}\left(\frac{\partial\epsilon}{\partial P}\right)^2_{T,\rho_2} \qquad \text{(2-27}$$

Using an equation of the form of (2-1) yields the ratio of the intensity of the Brillouin peaks to the incident light from equation (2-27). However, a more useful form exists. The entire dielectric fluctuation is, in terms of fluctuations of the state variables, T, P, and ρ_2,

$$\langle(\Delta\epsilon)^2\rangle = \left(\frac{\partial\epsilon}{\partial T}\right)^2_{P,\rho_2} \langle(\Delta T)^2\rangle + 2\left(\frac{\partial\epsilon}{\partial T}\right)_{P,\rho_2}\left(\frac{\partial\epsilon}{\partial P}\right)_{T,\rho_2}\langle\Delta T\Delta P\rangle$$

$$+\left(\frac{\partial\epsilon}{\partial P}\right)^2_{T,\rho_2}\langle(\Delta P)^2\rangle + \left(\frac{\partial\epsilon}{\partial\rho_2}\right)^2_{T,P}\langle(\Delta\rho_2)^2\rangle \qquad (2\text{-}28$$

Here, only one of the three cross terms is non-zero. From equations (2-24a-e), this can be converted to

$$\langle(\Delta\epsilon)^2\rangle = \frac{kT^2}{C_V}\left(\frac{\partial\epsilon}{\partial T}\right)^2_{P,\rho_2} + \frac{2kT^2\alpha_P}{\kappa_T C_V}\left(\frac{\partial\epsilon}{\partial T}\right)_{P,\rho_2}\left(\frac{\partial\epsilon}{\partial P}\right)_{T,\rho_2}$$

$$+\frac{kT}{V\kappa_S}\left(\frac{\partial\epsilon}{\partial P}\right)^2_{T,\rho_2} + kT\left(\frac{\partial\epsilon}{\partial\rho_2}\right)^2_{T,P}\bigg/\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T,P} \qquad (2\text{-}29$$

The contribution to the central or Rayleigh peak is given by

$$\langle(\Delta\epsilon)^2_C\rangle = \langle(\Delta\epsilon)^2\rangle - \langle(\Delta\epsilon)^2_{ADIAB}\rangle \qquad (2\text{-}30$$

Subtracting (2-27) from (2-29) leads to

$$\langle(\Delta\epsilon)^2_C\rangle = \frac{kT^2}{C_V}\left(\frac{\partial\epsilon}{\partial T}\right)^2_{P,\rho_2} + kT\left(\frac{\partial n}{\partial\rho_2}\right)^2_{T,P}\bigg/\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T,P} \qquad (2\text{-}31$$

Because the ratio of the Rayleigh to the Brillouin peaks allows the use of two intensities that are more similar than those of scattered to incident light, their ratio, J, is used.

$$J = i_C / 2\, i_B = \langle(\Delta\epsilon)^2_C\rangle / \langle(\Delta\epsilon)^2_{ADIAB}\rangle \qquad (2\text{-}32$$

Defining the variable f in terms of $x^{(1)}$ from equation (2-6) (Miller and Lee, 1968) gives

$$f = \frac{2x^{(1)}}{1 - x^{(1)}} + \frac{\gamma_C\,[x^{(1)}]^2}{(1 - x^{(1)})^2} \qquad (2\text{-}33$$

Equation (2-32) can be rewritten to include both the temperature and pressure derivatives of the refractive index

$$J = \frac{\gamma_C - 1}{1 + f\gamma_C} + \frac{C_P}{T}\,(\gamma_C - 1)\,x_1 \left(\frac{\partial n}{\partial x_2}\right)_T^2 \Bigg/ \left[\left(\frac{\partial n}{\partial T}\right)_P^2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} (1 + f\gamma_C)\right] \qquad (2\text{-}34$$

where

$$\gamma_C = \frac{C_P}{C_V} \qquad (2\text{-}35$$

Often (Miller, 1967; Coumou and Mackor, 1964), it is assumed that $x^{(1)} = 0$, giving

$$J = \gamma_C - 1 + \frac{C_P}{T}\,(\gamma_C - 1)\,x_1 \left(\frac{\partial n}{\partial x_2}\right)^2 \Bigg/ \left[\left(\frac{\partial n}{\partial T}\right)_P^2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}\right] \qquad (2\text{-}36$$

The equation connecting light scattering data to thermodynamic properties is (2-34) or (2-36). It assumes that there are no internal molecular relaxation processes that contribute to the scattering. Unfortunately, this is not normally the case.

Light Scattering in Relaxing Solutions

Miller and Lee (1968) noted that internal molecular relaxations in a liquid can transfer energy from the central to the outer peaks. Fishman and Mountain (1970) showed how to correct the dynamic changes in pressure, temperature and concentration for this effect using linearized hydrodynamic equations for momentum, energy and diffusion transport. Miller and Lee (1973) implemented the Fishman and Mountain expressions to find the portion of the scattered light transferred from the side peak to the central peak, (Δ_i). Then, the measured ratio of the Rayleigh to the Brillouin peaks, J(k), becomes

$$J(k) = \frac{J(0) + \Delta_i}{1 - \Delta_i} \qquad (2\text{-}37$$

where J(0) is the ratio to be used in equations (2-34) and (2-36), and Δ_i is

$$\Delta_i = A(k)\, J(0) + B(k) \qquad \text{(2-38}$$

with

$$A(k) = \left[(v_\infty^2 - v_S^2)\, k_V^2\, \tau^2 + \left(\frac{v_o}{v_S}\right)^4 - \left(\frac{v_o}{v_S}\right)^2 \right] \Big/ \left[(v_S k_V \tau)^2 + \left(\frac{v_o}{v_S}\right)^4 \right] \qquad \text{(2-39a}$$

$$B(k) = \left[(v_\infty^2 - v_o^2)\, k_V^2\, \tau^2 + \left(\frac{v_o}{v_S}\right)^4 - \left(\frac{v_o}{v_S}\right)^2 \right] \Big/ \left[(v_S k_V \tau)^2 + \left(\frac{v_o}{v_S}\right)^4 \right] \qquad \text{(2-39b}$$

Here, the physical quantities are

v_∞: infinite frequency velocity of sound

v_o: zero frequency velocity of sound

v_S: velocity of sound in solution

τ: single relaxation time for the internal degrees of freedom

k_V: change in wave vector by the relaxation

The value of v_S can be determined from the frequency shift, or the separation, $\Delta\upsilon$, between the Rayleigh and Brillouin peaks.

$$v_S = \frac{c\Delta\upsilon}{2\upsilon \sin(\theta/2)} \qquad \text{(2-40}$$

where the additional physical properties are

υ: frequency of incident light

c: speed of light

θ: scattering angle

The value of k_V can be obtained from the incident light wave length λ_o and θ.

$$k_V = \left(\frac{4\pi n}{\lambda_o}\right) \sin(\theta/2) \qquad \text{(2-41}$$

The ratio of scattered peaks, J(0), for use in equations (2-34) or (2-36) can be written in terms of the measured ratio, J(k) and the relaxation functions, A(k) and B(k):

$$J(0) = \frac{J(k)\,[1 - B(k)] - B(k)}{1 + A(k) + J(k)\,A(k)} \tag{2-42}$$

Combination of equations (2-42) and (2-34) gives a completely rigorous treatment.

Fishman and Mountain (1970) point out that A(k) is small and can sometimes be neglected, allowing measurement of J(k) at several angles to be used to establish B(k) and J(0) simultaneously. This eliminates the need for relaxation data but requires a light scattering apparatus that can measure scattering at different angles. An alternative simplification was attempted by Miller and Lee (1973). They ignore A(k) and force τ, v_∞ and v_o to vary linearly with concentration. They then obtain

$$J(k) = \gamma_C\, r - 1 + (\gamma_C - 1)\, r\, K\, x_1\, x_2 \Big/ \left[1 + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \right] \tag{2-43}$$

where

$$r = \frac{v_S^2}{v_o^2} \tag{2-44a}$$

$$K = \frac{C_P}{RT^2} \left[\left(\frac{\partial n}{\partial x_2} \right) \Big/ \left(\frac{\partial n}{\partial T} \right)_P \right]^2 \tag{2-44b}$$

This more general treatment arrives at equations (2-42) and (2-34) without approximations. There are four different treatments available to relate light scattering to thermodynamic properties. Three of the four methods involve approximations which can lead to different results, but require less input data. Our objective was to do the most complete analysis possible and determine what quantitative information can be obtained while listing the total amount of input information required for such a treatment.

Calculation of Thermodynamic Properties

Fluctuation Properties

Recently, several authors (Iwasaka et al., 1976; Kato et al., 1982; Kato and Fujiyama, 1976; Kato, 1984) have used the early theory of Miller (1967) to describe the concentration fluctuations in solutions from light scattering measurements. Iwasaka, et al. (1976) calculated the concentration fluctuations, $V\langle(\Delta x_2)^2\rangle$ by solving for $\langle(\Delta\rho_2)^2\rangle$ in equation (2-28) for the system, CCl_4 / CS_2. Miller and Lee (1968; 1973) indicated that both these substances are relaxing fluids, an effect ignored by Iwasaka and Kato. Kato (1984) calculated the Kirkwood-Buff (1951) integrals over the total correlation function from chemical potential derivatives and other fluctuation properties. As we establish in more detail later, the stated accuracy of about 10% in the light scattering measurement is not sufficient for determination of reliable chemical potential derivatives, even when relaxation is included. In fact, without consideration of relaxation effects, the results are expected to be seriously in error.

Activity Coefficients

Most investigators ultimately use a formulation to calculate solution activity coefficients. The relationship of most generality and utility for the activity coefficient derivative is

$$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)_{T,P} = \left(\frac{\gamma_C - 1}{1 + f\gamma_C}\,\frac{C_P x_1}{RT^2}\left[\left(\frac{\partial n}{\partial x_2}\right)\Big/\left(\frac{\partial n}{\partial T}\right)_P\right]^2\Big/\left[J(0) - \frac{\gamma_C - 1}{1 + f\gamma_C}\right]\right) - \frac{1}{x_2} \qquad (2\text{-}45$$

where J(0) is defined by equation (2-42). The most recent use of this complete theory of Miller and Lee and of Fishman and Mountain is that of Maguire et al. (1981), who used J(0) values from light scattering to obtain activity coefficients and excess Gibbs energies to compare with those from experimental vapor-liquid equilibrium data.

The activity coefficient can be calculated from

$$\ln\gamma_2 = \int_{x_2}^{1} \left(\frac{1}{x_2} - \left(\left[J_{ID} - \frac{\gamma_C - 1}{1 + f\gamma_C} \right] \bigg/ \left[J(0) - \frac{\gamma_C - 1}{1 + f\gamma_C} \right] \right) \bigg/ x_2 \right) dx_2 \qquad \text{(2-46}$$

The quantity, J_{ID}, is a convenient grouping of variables that resembles J(0) for an ideal solution:

$$J_{ID} = \frac{\gamma_C - 1}{1 + f\gamma_C} \left(1 + \frac{C_P x_1 x_2}{RT^2} \right) \left[\left(\frac{\partial n}{\partial x_2} \right) \bigg/ \left(\frac{\partial n}{\partial T} \right)_P \right]^2 \qquad \text{(2-47}$$

where f is defined by equation (2-33). This is not the actual J(0) for an ideal solution because there are still many data in J_{ID} that are dependent on the composition of the real solution.

For comparison to vapor-liquid equilibria data, equation (2-34) can be used with chemical potential derivatives calculated from VLE data to compare with J(0), (J_{THERM}).

Before discussing the results of the calculations by Maguire et al. (1981) and their consequences, we recapitulate in detail the elaborate procedure and extensive set of property values required to obtain activity coefficients from light scattering data. We also duplicate their calculations for the cyclohexane/benzene system, which was chosen because most of the data have been measured. In other systems, approximations would be required, leading to greater errors, we believe.

Activity Coefficients from Equation (2-46)

Listed below are the calculational steps used by Maguire et al. (1981) to obtain the activity coefficients and excess Gibbs energies for the cyclohexane/benzene system. In cases of ambiguity in the publication, we state our assumptions about what was done.

1. $J(k)$ from measured light scattering, at T, P, x (Table 2-1, Column 2)
   - From Table II of Maguire et al. (1981).
   - Assumed $P = 1$ bar, $T = 296$ K as in Brown et al. (1978).
2. k_V from equation (2-41) (Table 2-1, Column 3)
   - a. Refractive index, n, at T, x (Table 2-1, Column 4).

     Interpolated from Table 4 of Brown et al.(1978)
   - b. Wavelength of incident light, λ_o.
     - Assumed to be that of Brown et al. (1978), 5.46×10^{-7} m.
   - c. Scattering angle, θ.
     - Assumed to be 90 degrees.
3. v_S, from equation (2-40) (Table 2-1, Column 5)
   - a. Frequency of Brillouin Shift, $\Delta\upsilon$ not reported.
     - Used Figure 4 for $v_S(k)$ vs. composition of

       Maguire et al.(1981). Table 2-2 lists values read off graph.

       Values linearly interpolated to Table 2-1 compositions.
4. $A(k)$ and $B(k)$ from equations (2-39a,b) (Table 2-1, Columns 6 and 7)
   - a. v_∞ at T, x. (Table 2-1, Column 8)
     - Pure benzene from measurements of Eastman et al. (1969).
     - Pure cyclohexane calculated using $A(k)$ from Figure 3,

       $J(0)$ and $J(k)$ from Table I, all from Maguire et al. (1981),

       and $B(k)$ calculated using equation (2-42).

       Final value calculated from equation (2-39b).
     - Linear composition dependence assumed.
   - b. v_o at T, x (Table 2-1, column 9)
     - Pure benzene from measurements of Eastman et al. (1969).
     - Pure cyclohexane from measurements of Dorfmuller et al. (1976).

Table 2-1
Physical Properties Needed for Light Scattering Analysis
of Cyclohexane(1)/Benzene(2) Solutions

x_2 1	J(k) 2	k_V m^{-1} x 10^{-7} 3	n 4	v_S m/s 5	A(k) 6	B(k) 7	v_∞ m/s 8	v_o m/s 9	τ sec x 10^{11} 10
0.000	0.55	2.32	1.4285	1345.0	0.0166	0.0795	1395.7	1280.0	4.10
0.102	0.68	2.33	1.4321	1345.0	0.0391	0.0995	1411.5	1284.5	4.30
0.202	0.92	2.34	1.4366	1347.1	0.0588	0.1184	1426.9	1288.9	4.49
0.296	1.07	2.35	1.4412	1351.8	0.0736	0.1352	1441.4	1293.0	4.68
0.304	1.09	2.35	1.4417	1352.5	0.0744	0.1365	1442.6	1293.4	4.69
0.350	1.23	2.35	1.4442	1358.5	0.0764	0.1434	1449.7	1295.4	4.78
0.488	1.38	2.36	1.4532	1382.6	0.0738	0.1623	1471.0	1301.5	5.05
0.651	1.46	2.39	1.4656	1420.2	0.0584	0.1824	1496.2	1308.6	5.37
0.747	1.41	2.40	1.4739	1444.1	0.0474	0.1939	1511.0	1312.9	5.56
0.850	1.29	2.41	1.4836	1480.0	0.0222	0.2031	1526.9	1317.4	5.76
0.900	1.16	2.42	1.4887	1500.0	0.0071	0.2068	1534.6	1319.6	5.86
1.000	0.90	2.44	1.4990	1540.0	-0.0219	0.2140	1550.0	1324.0	6.05

Table 2-1 Continued

x_2 1	J(0) 11	J(0)† 12	J_{ID} 13	f x 10^2 14	C_P J/molK 15	$\left(\frac{\partial n}{\partial x_2}\right)$ 16	$\left(\frac{\partial n}{\partial P}\right)$ Pa^{-1} x 10^{10} 17	γ_c-1 18	$\left(\frac{\partial n}{\partial T}\right)$ K^{-1} x 10^4 19	κ_T Pa^{-1} x 10^9 20	α_P K^{-1} x 10^3 21
0.000	0.416	0.378	0.378	-1.47	155.0	0.0314	5.08	0.3700	-5.38	1.15	1.21
0.102	0.481	0.436	0.410	0.48	153.1	0.0394	5.12	0.3751	-5.46	1.13	1.21
0.202	0.623	0.571	0.458	2.24	151.2	0.0472	5.16	0.3801	-5.54	1.12	1.21
0.296	0.686	0.628	0.510	4.26	149.4	0.0546	5.20	0.3848	-5.61	1.10	1.21
0.304	0.696	0.638	0.513	4.64	149.2	0.0552	5.21	0.3852	-5.62	1.10	1.21
0.350	0.778	0.717	0.530	7.01	148.4	0.0588	5.24	0.3875	-5.66	1.08	1.21
0.488	0.845	0.776	0.616	7.55	145.7	0.0696	5.27	0.3944	-5.77	1.07	1.21
0.651	0.884	0.804	0.673	7.99	142.6	0.0823	5.29	0.4026	-5.93	1.04	1.21
0.747	0.846	0.760	0.669	7.38	140.8	0.0898	5.27	0.4074	-6.02	1.02	1.21
0.850	0.785	0.692	0.622	5.22	138.9	0.0979	5.24	0.4125	-6.14	1.01	1.21
0.900	0.703	0.606	0.571	4.24	137.9	0.1018	5.24	0.4150	-6.21	1.00	1.21
1.000	0.515	0.412	0.412	1.35	136.0	0.1096	5.23	0.4200	-6.38	0.99	1.21

†J(0) Adjusted to Match J_{ID} at Pure Components

- Linear composition dependence assumed.

c. τ at T, x (Table 2-1, column 10).

- Pure benzene calculated using A(k) from Figure 3 and J(0) and J(k) from Table I, all from Maguire et al. (1981), and B(k) was calculated using equation (2-42). Final value calculated from equation (2-39b).
- Pure cyclohexane from measurements of Dorfmuller et al. (1976).
- Linear composition dependence assumed.

5. f from equation (2-33) (Table 2-1, Column 14)

- $x^{(1)}$ from equation (2-5).

6. J(0) from equation (2-42) (Table 2-1, Columns 11 & 12)

- Calculated values, Column 11.
- Linearly adjusted to match pure component J_{ID}, Column 12

7. J_{ID} from equation (2-47) (Table 2-1, Column 13)

a. C_p at T, x (Table 2-1, Column 15)

- Pure component values from Table III, Maguire et al. (1981)
- Linear composition dependence assumed.

b. $\left(\frac{\partial n}{\partial x_2}\right)_T$ (Table 2-1, column 16)

- Analytical equation of Brown et al. (1978)

c. $\left(\frac{\partial n}{\partial P}\right)_{T,x}$ (Table 2-1, Column 17).

- Interpolated from Table 4, Brown et al. (1978)

d. $(\gamma_C - 1)$ or $(C_P - C_V)/C_V$ at T, x (Table 2-1, column 18)

- Pure component values from Table I, Maguire et al. (1981).
- Linear composition dependence assumed.

e. $\left(\frac{\partial n}{\partial T}\right)_{P,x}$ (Table 2-1, Column 19)

- Interpolated from Table 2, Coumou and Mackor (1964).

f. κ_T (Table 2-1, Column 20)

- Pure component data from Table III, Maguire et al. (1981).
- Linear composition dependence assumed.

g. α_P at T, x (Table 2-1, Column 21)

- Pure component data from Table III, Maguire et al. (1981)
- Linear composition dependence assumed.

8. Activity coefficients from equation (2-46) (Table 2-3, Column 3)

- The integral was calculated using a trapezoidal rule.
- Experimental data of Nagata (1962) (Table 2-3, Column 2)

Table 2-2
Speed of Sound in Cyclohexane/Benzene Mixtures
at 296 K and 1 atm

x_2	v_S m/s	x_2	v_S m/s
0.0	1345	0.6	1410
0.1	1345	0.7	1430
0.2	1347	0.8	1460
0.3	1352	0.9	1500
0.4	1365	1.0	1540
0.5	1385		

Comparisons with Phase Equilibrium Measurements

After duplicating the calculations of Maguire et al. (1981) in this way, a quantitative comparison can be made of this method with vapor-liquid equilibrium measurements. The values of $\ln\gamma_2$ are shown in Figure 2-1 and listed in Table 2-3. The absolute average error is 0.25 or 25% in the activity coefficient. However, much greater errors occur at low concentrations because the integration in equation (2-46) accumulates errors. We expect that the results are not within the experimental accuracy of the vapor-liquid equilibrium measurements, which should be correct to within 2%. Figure 2-2 shows the scattering J(0) compared with J_{THERM} from analysis

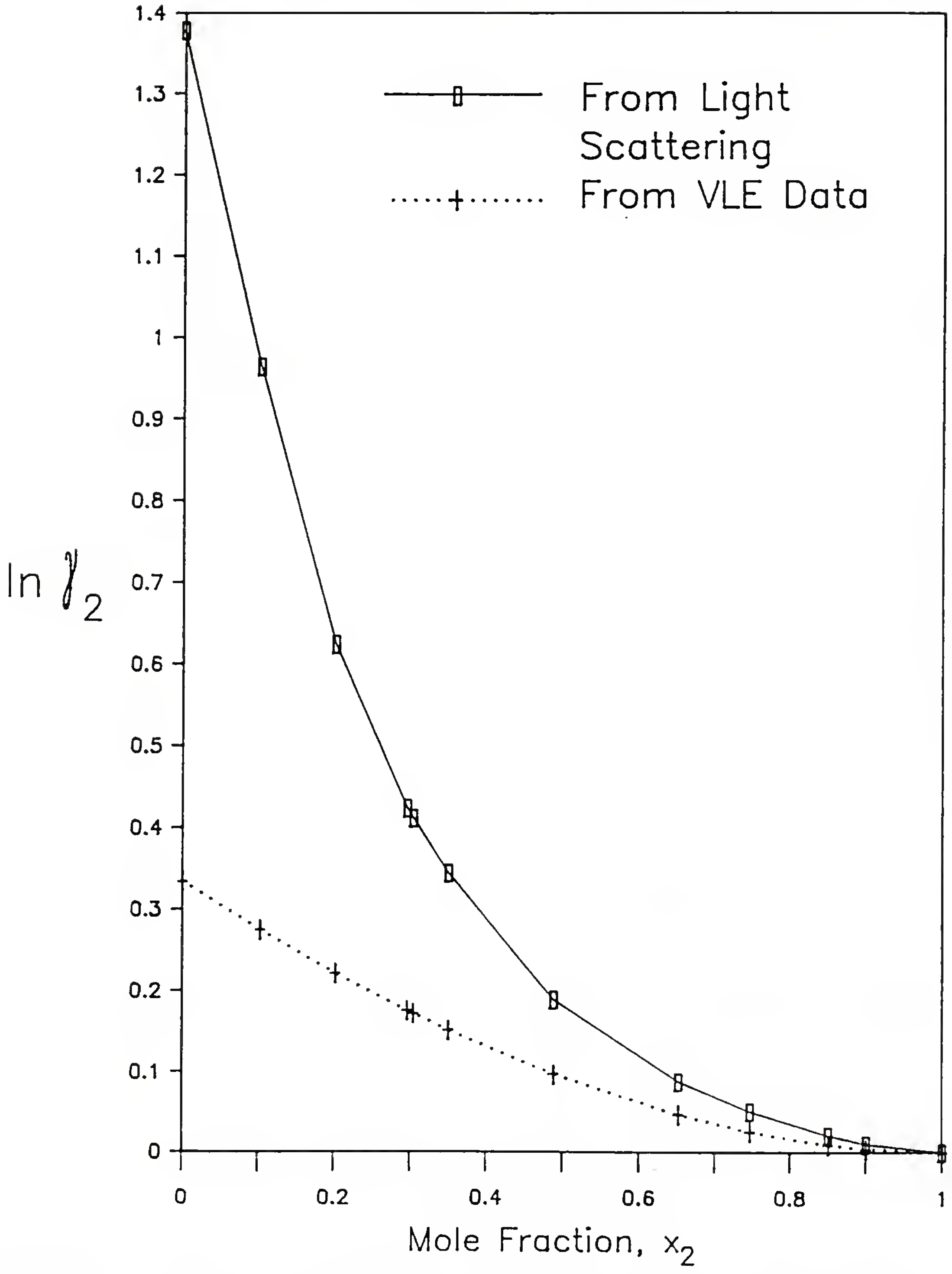

Figure 2-1 Activity Coefficients Calculated From Vapor-Liquid Equilibrium Data of Nagata (1962) and From Light Scattering Data For the Cyclohexane(1) / Benzene(2) System at 23° C.

of the vapor-liquid equilibrium measurements (Table 2-3, Column 6). These have an average absolute difference of 0.035 or 5% which leads to the 0.25 average difference in $\ln\gamma_2$.

Table 2-3
Comparison of Activity Coefficients From
Light Scattering and Vapor-Liquid Equilibrium Data
For the System Cyclohexane(1)/Benzene(2) at 296 K

x_2 1	$\ln\gamma_2$ from VLE† 2	$\ln\gamma_2$ from light scatter data 3	$\ln\gamma_2$ abs. diff 4	$\left(\frac{\partial\ln\gamma_2}{\partial x_2}\right)$ from VLE† 5	J_{THERM} from VLE† 6
0.000	0.335	1.378	1.043	-0.607	0.378
0.102	0.275	0.965	0.689	-0.561	0.412
0.202	0.222	0.624	0.403	-0.513	0.469
0.296	0.176	0.424	0.248	-0.465	0.533
0.304	0.172	0.412	0.240	-0.461	0.538
0.350	0.151	0.344	0.192	-0.436	0.562
0.488	0.096	0.188	0.092	-0.358	0.670
0.651	0.046	0.087	0.041	-0.256	0.735
0.747	0.025	0.050	0.026	-0.191	0.719
0.850	0.009	0.021	0.012	-0.117	0.648
0.900	0.004	0.009	0.005	-0.079	0.584
1.000	0.000	0.000	0.000	0.000	0.412

† Nagata (1962)

Sensitivity of Activity Coefficient Calculations

To determine the effect of uncertainties in the light scattering measurements, an additive random error was introduced into the J(k) values and these were used in a second set of calculations

$$J(k)_{ERROR} = J(k)_{EXPT} + F \times N_R \qquad \text{(2-48}$$

where $J(k)_{EXPT}$ is the measured J(k) and N_R is a random number between -0.5 and 0.5. The factor, F, was adjusted until the standard deviation of the error between the

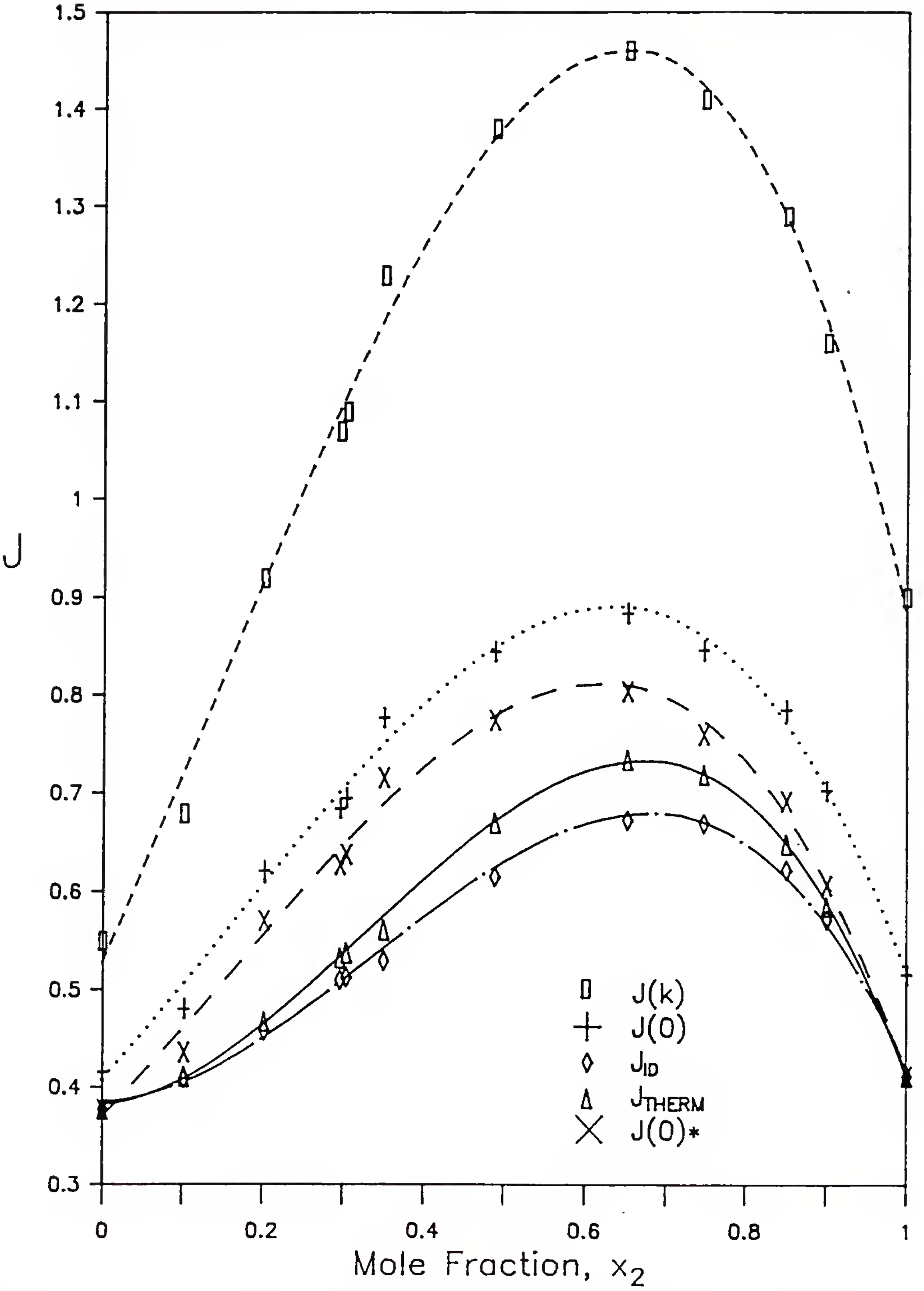

Figure 2-2 Various Rayleigh to Brillouin Scattering Ratios (J) For the Cyclohexane(1) / Benzene(2) System at 23° C.

$J(k)_{ERROR}$ and $J(k)_{EXPT}$ was either 0.05 or 0.10. The 12 random number values used had an average of -0.113. This means that we introduced both random and systematic errors.

The results of this numerical experiment are given in Figures 2-3 and 2-4 for the calculated J(0) and $\ln\gamma_2$ while Table 2-4 summarizes the results for the compositions of Table 2-1. Part of the errors in J(k) are passed on to J(0) and, subsequently to $\ln(\gamma_2)$. Since other input parameters, such as the speed of sound in the solution or the relaxation parameters, may be difficult to find, we vary these individually by 5-20% so their impact on J(0) and $\ln(\gamma_2)$ can be detected. Table 2-5 shows that rough approximations to these parameters, particularly for v_∞, τ and B(k), will not be good enough for obtaining activity coefficients as accurately as from vapor-liquid equilibrium data.

Table 2-4
Errors in J(0) and $\ln\gamma_2$ Caused by Random Errors in J(k)

Standard Deviation of Random Error in J(k)	Standard Deviation in Error J(0)	Average Absolute Error Calculated $\ln\gamma_2$
0.00	0.041	0.249
0.05	0.046	0.243
0.10	0.092	0.598

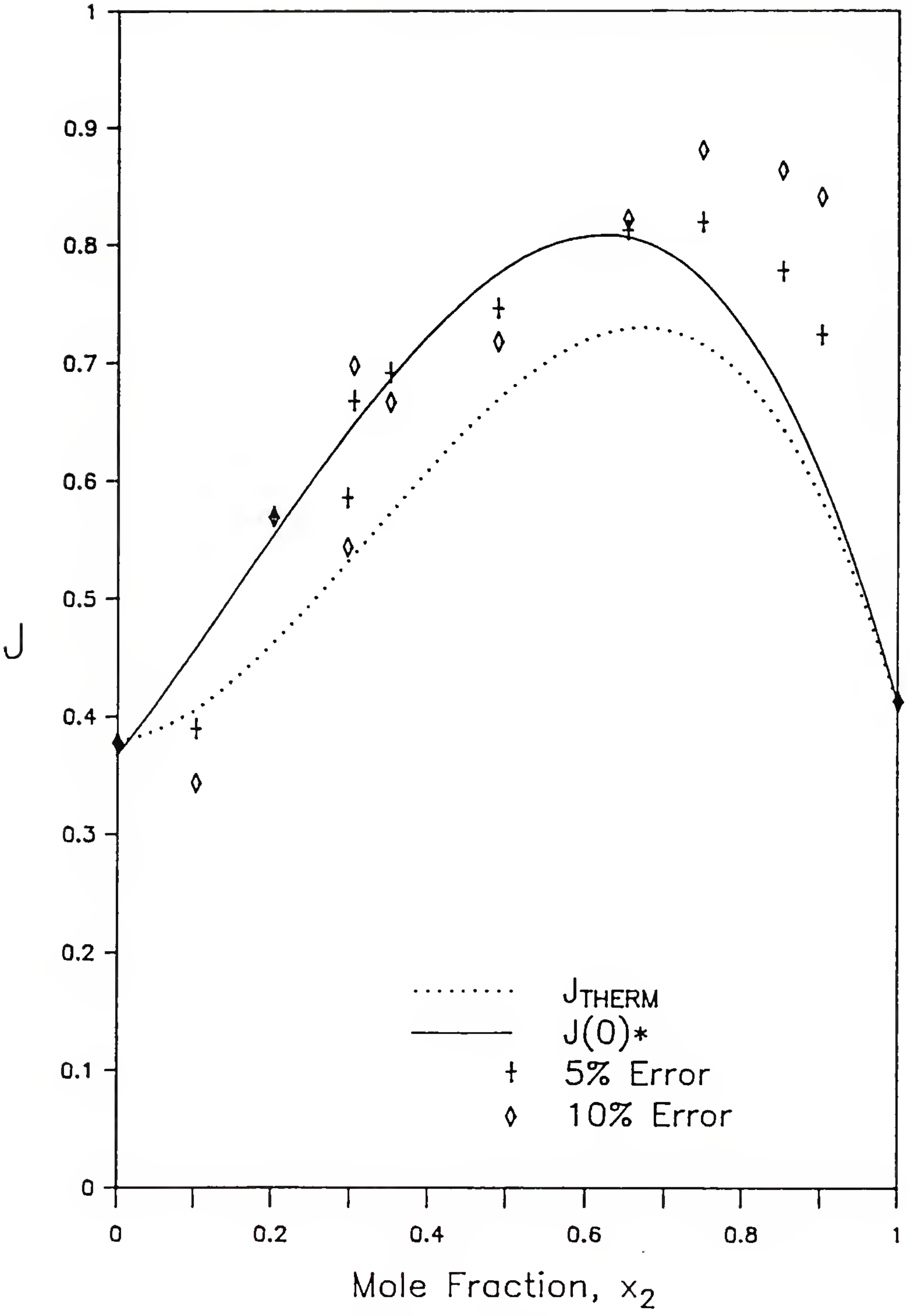

Figure 2-3 Values of J(0)* Calculated From Measured Values of J(k) For the System Cyclohexane(1) / Benzene(2) With Various Random Errors Added at 23° C.

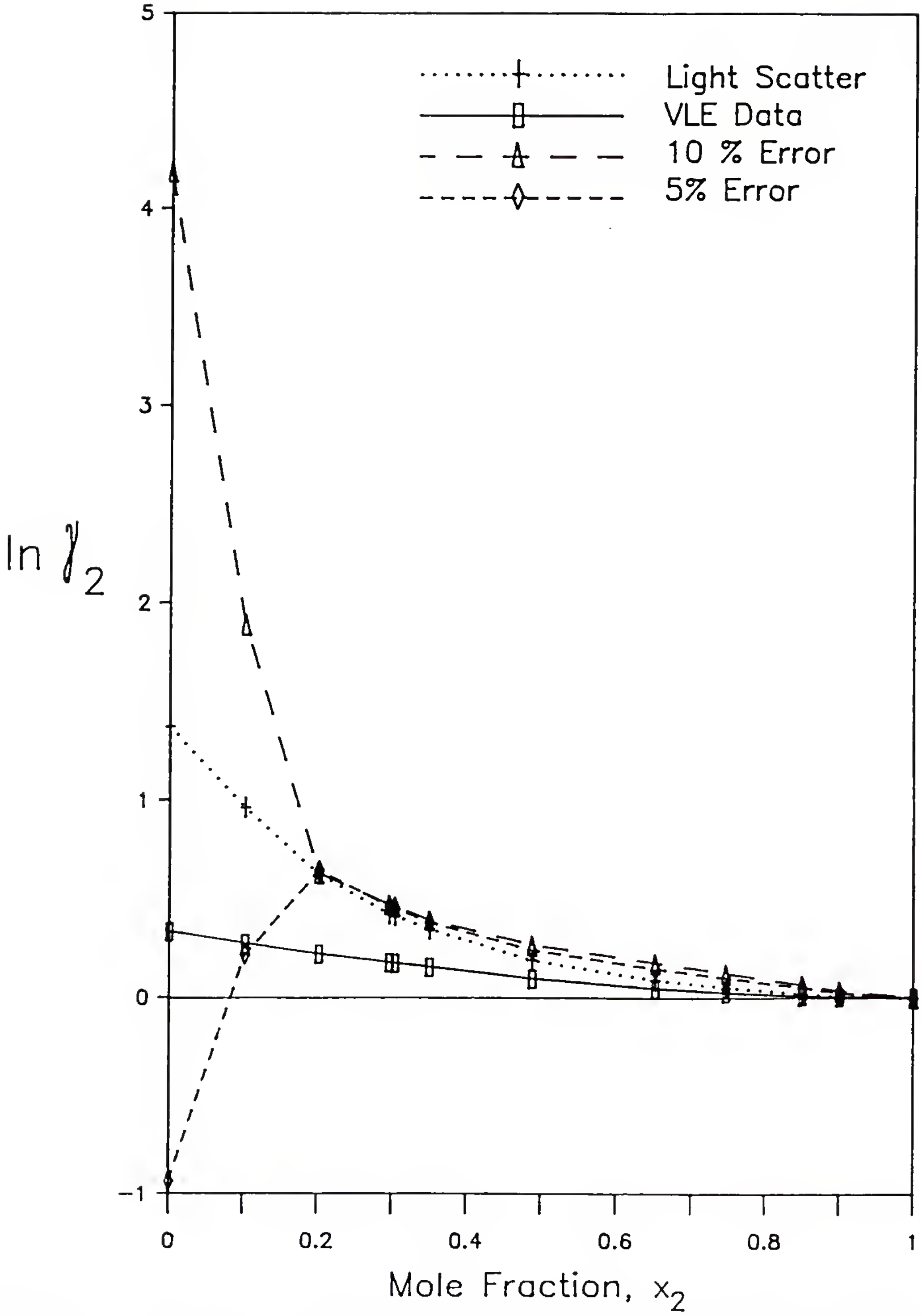

Figure 2-4 Activity Coefficient in the Cyclohexane(1) / Benzene(2) System Calculated from Light Scattering, With Various Random Errors Added to J(0)*.

Table 2-5
Error in $\ln\gamma_2$ Caused by Bad Input Values

	Errored Inputs (%†)	Table 1 Values	Standard Deviation In Error of J(0)	Average Absolute Error $\ln\gamma_2$
All Original Values	-	-	0.033	0.249
Cyclohexane v_o	1100 (-15)	1280	0.063	0.330
Cyclohexane v_∞	1600 (+15)	1395	0.047	0.366
Cyclohexane τ	$1x10^{-11}$	$4.1x10^{-11}$	0.160	2.02
Cyclohexane τ	$1x10^{-10}$	$4.1x10^{-11}$	0.036	0.215
Benzene B(k)	0.205 (-4)	0.214	0.032	0.260
Benzene B(k)	0.225 (+4)	0.214	0.035	0.229
Cyclohexane B(k)	0.0625(-20)	0.0795	0.037	0.275
Cyclohexane B(k)	0.095 (+20)	0.0795	0.030	0.224

† Deviations from Table 1 Values

Summary

The measurement of concentration fluctuations from light scattering is a possible route for obtaining activity coefficients. An investigation was made of cyclohexane/benzene, a typical organic system, for which all necessary data for the rigorous analysis, including relaxation information, were available. The results are seriously in error from reliable vapor-liquid equilibrium data.

Miller and Lee (1973) state that large excess scattering (solution scattering over pure component values) is needed to obtain activity coefficients. They point out that systems with a pure component refractive index greater than 0.2 are required for reliable results. For pure components here, J(0) is approximately γ_C - 1 (the Landau-Placzek formula). The difference between the maximum J(0) observed for the cyclohexane/benzene system and γ_C - 1 is approximately 0.40, evidently not great enough to reliably determine activity coefficients. Miller and Lee (1973) indicate that in systems with large pure component refractive index differences ($\Delta n > 0.2$) the excess scattering can be adequate.

The results of this analysis, where $\Delta n \simeq 0.07$, are consistent with the prediction of Miller and Lee. The activity coefficients of the cyclohexane/benzene system cannot be determined by light scattering even if all information is available. If the ancillary information is erroneous, it is clear that the sensitivity of the results makes light scattering unlikely to be viable for determination of activity coefficient derivatives in any system. Finally, it should also be noted that instrument expense and dust-free sample preparation are not insignificant factors to be considered in the light-scattering experiment.

It might be appropriate to test the method with a system having $\Delta n > 0.2$ for which all the auxiliary properties are available in order to determine the real possibilities of the technique. However, such a high refractive index difference requirement would limit the number of real systems so severely that another measurement must be sought. Equilibrium sedimentation in an ultracentrifuge is such a technique. As discussed in the next chapter, it can be used for systems where $\Delta n > 0.06$ and the extra required information is much less.

CHAPTER 3

CONCENTRATION DERIVATIVES OF DILUTE SOLUTION ACTIVITY COEFFICIENTS USING AN ANALYTICAL ULTRACENTRIFUGE

Introduction

While light scattering is apparently not accurate enough to provide useful information about solution activity coefficients, other possibilities besides traditional vapor-liquid equilibrium (VLE) measurements (Gmehling et al., 1977, Wichterle et al., 1973) need to be explored. In particular, accurate measurements need to be made in the 2.5% to 10% (mole) range to determine activity coefficients and their composition derivatives more accurately. Data in this region are of interest because, as Loblen and Prausnitz (1982) and Schreiber and Eckert (1971) point out, extrapolations of finite concentration VLE data to infinite dilution do not usually agree with the direct measurements of γ^{∞} by differential ebulliometry and chromatography. For example, Figure 3-1 shows VLE data for the carbon disulfide/acetone system (Litvinov, 1952) fit to the Wilson (1964), NRTL (Renon and Prausnitz, 1968) and Margules (Van Ness and Abbott, 1982) activity coefficient models. Clearly, all of the models fit the mid-range concentration data equally well. However, at low concentrations, the three equations deviate from each another, the departure being characteristic of the equation.

The differences in these models are even more pronounced when examined at the derivative level. As seen in Figure 3-2, when the same VLE data are fit to different activity coefficient models, the compositional derivatives can be quite different. Here the Margules model is not even monotonic. Besides the sensitivity of activity coefficient derivatives to discriminate between models, such data lead directly to the theoretical quantities of fluctuation solution theory (Kirkwood and Buff, 1951;

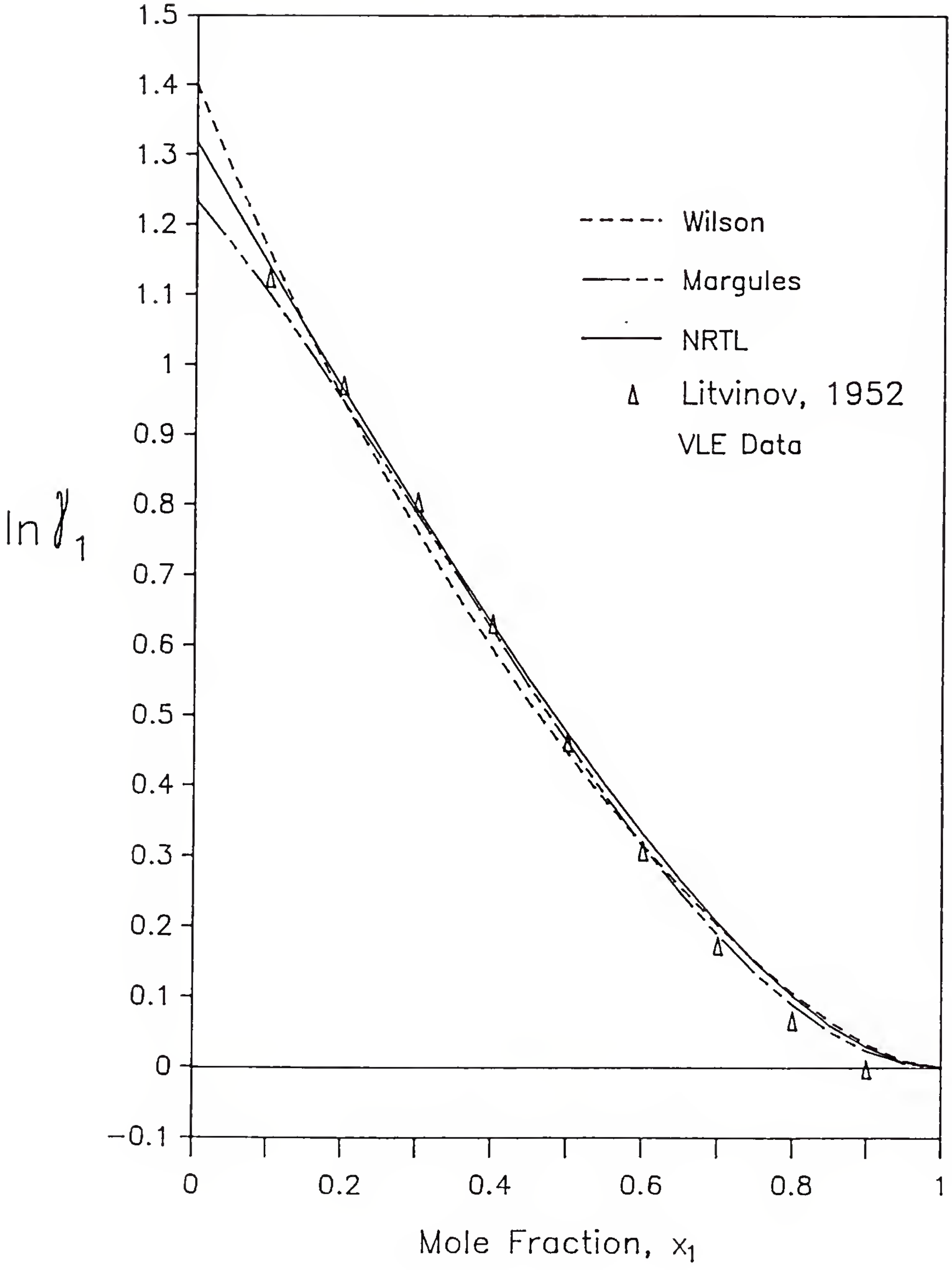

Figure 3-1 Various Activity Coefficient Models Fit to the VLE Data of Litvinov (1952) For the Carbon Disulfide(1) / Acetone(2) System at 25° C.

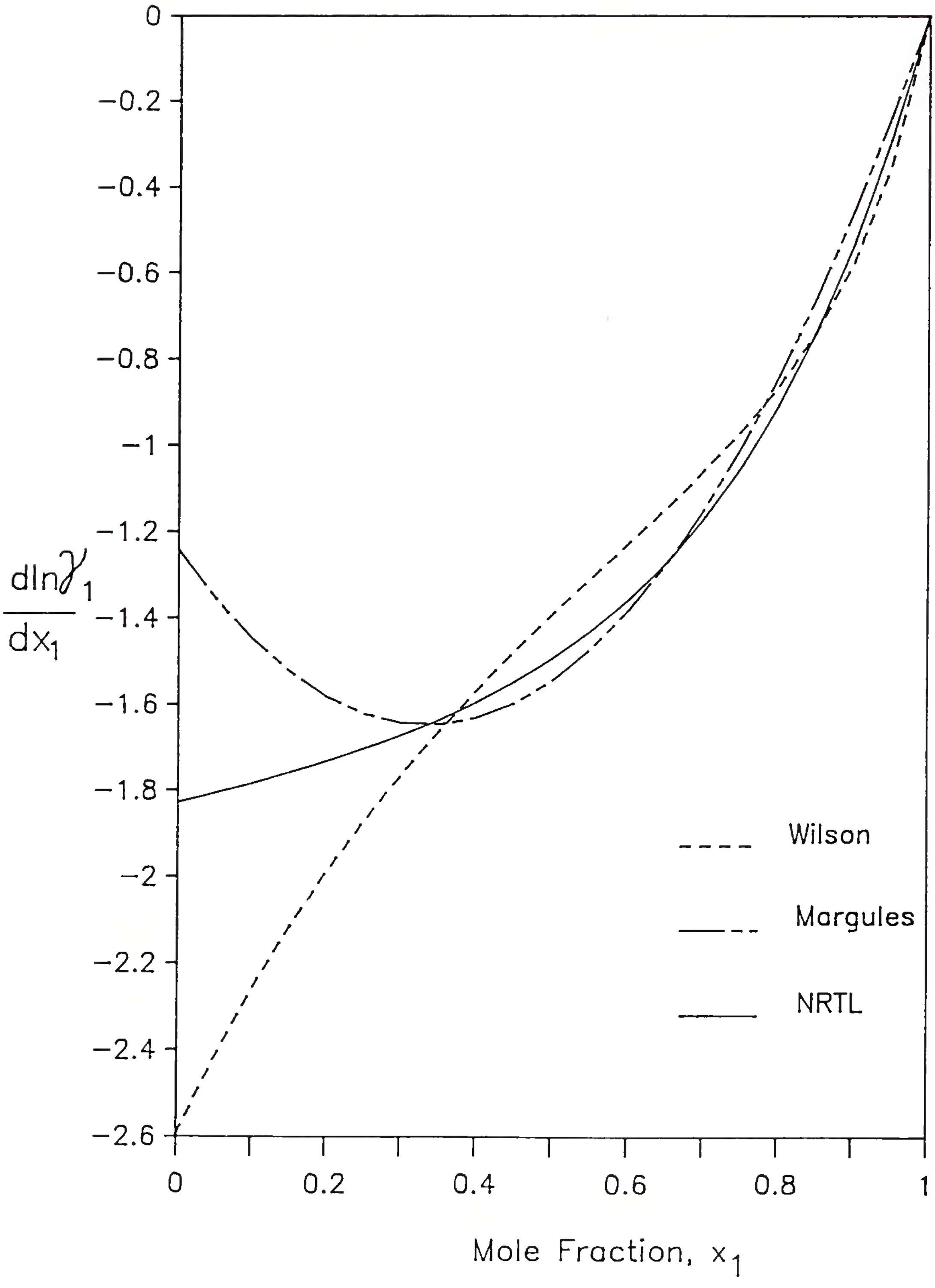

Figure 3-2 Activity Coefficient Derivatives From Various Models Using Parameters Fit to the VLE Data of Litvinov (1952). For the Carbon Disulfide (1) / Acetone (2) System at 25° C.

O'Connell, 1971; 1981; Campanella, 1984). In particular, integrals of the statistical mechanical direct correlation function (DCFI) can help future efforts toward solution models. For example, Campanella (1984) has noted that the derivatives of common activity coefficient models have a common mathematical form (ratios of polynomials in mole fraction). Such observations could lead to an accurate and general empirical activity coefficient model.

Thus, an experimental method which avoids use of a model and directly produces values of activity coefficient derivatives in dilute solution would be highly desirable. This would allow the determination of which, if any, of the activity coefficient models are most accurate and provide a basis for future models. Equilibrium sedimentation in an analytical ultracentrifuge provides such an experiment.

Equilibrium sedimentation distributes a heavier solute in a less dense solvent. Centrifugal force acts to push the heavier solute to the bottom of the cell. Diffusive forces tend to redistribute the solute. After a time these two forces balance each other and establish a compositional profile which is lower in the solute nearer the top of the cell. The experimental results are obtained from Rayleigh interference optics which gives composition profile while the sample is still in motion. A specially designed sample cell has two chambers or sectors, one is a reference which is filled with solvent while the other has the sample mixture. Laser light is split to shine through both chambers simultaneously. When recombined this light produces an interference pattern corresponding to the radial refractive index differences of the two cell chambers. The refractive index difference is directly related to the composition. An illustration of the sample cell and light path is given in Figure 3-3.

Initially the solution in the cell is homogeneous and the ultracentrifuge is operated in a steady fashion until equilibrium is established. After rotation starts, the time to reach a degree of equilibrium distribution (t_δ) is found from

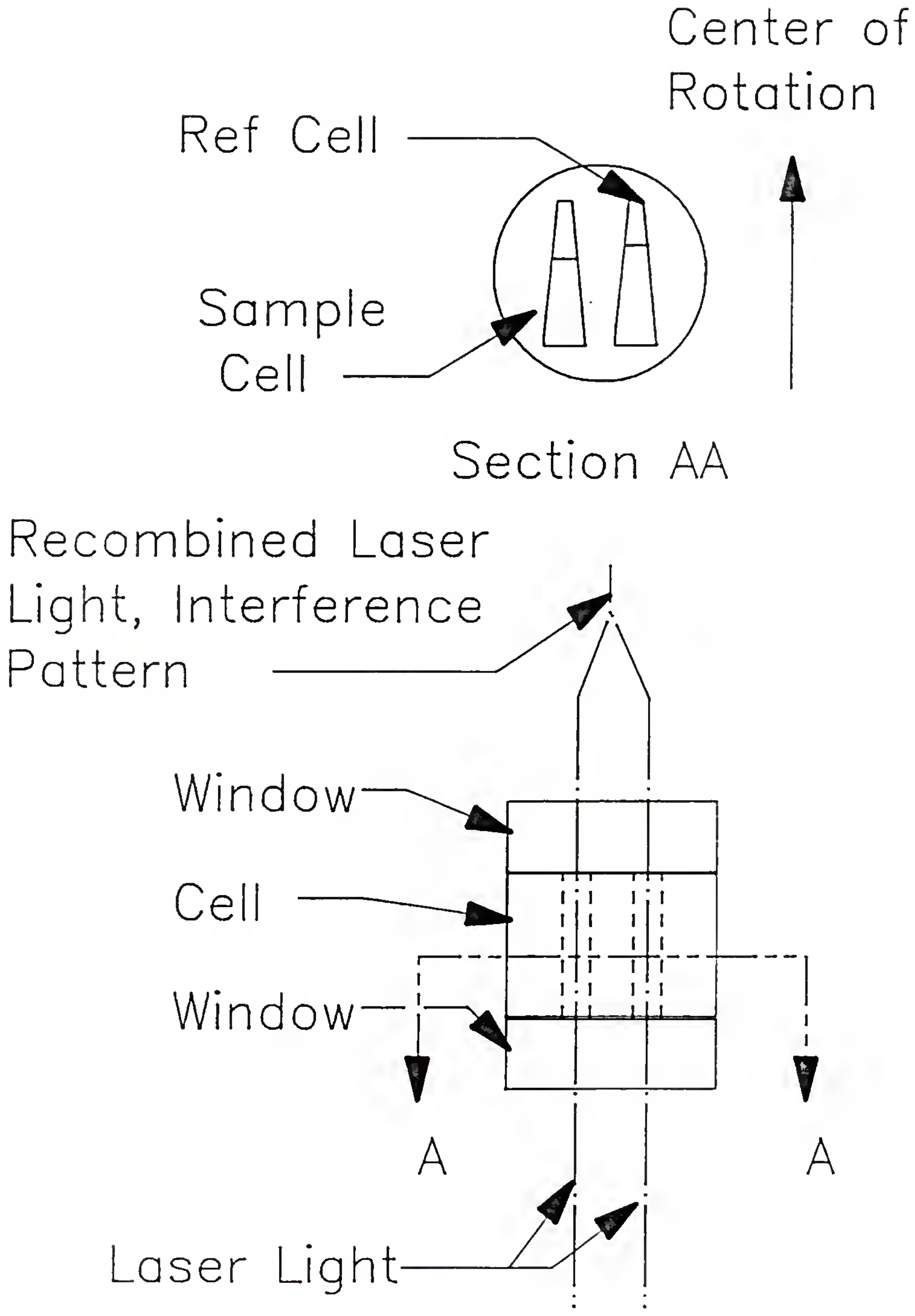

Figure 3-3 Ultracentrifuge Double Sectored Cell Showing the Location of the Sample Solution and Reference Solvent Relative to the Laser Light Path.

$$t_\delta = \frac{(\Delta r)^2}{4\pi^2 D} \ln \frac{2}{\pi^2(1 - \delta)} \tag*{(3-1}$$

where D is the diffusion coefficient and δ is the degree of equilibrium. For this experiment, a 99.9% degree of equilibrium ($\delta = 0.999$) can be considered adequate.

The solute (1) activity coefficient derivative is obtained from the isothermal derivative of the chemical potential being zero at equilibrium. In the ultracentrifuge the chemical potential is a function of distance of the solution from the axis of rotation, r, the pressure, P, and the mole fraction of solute, x_1.

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial r}\right)_{T,P,x_1} dr + \left(\frac{\partial \mu_1}{\partial P}\right)_{T,r,x_1} dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P,r} dx_1 = 0 \tag*{(3-2}$$

By substituting in known quantities for the partial derivatives, writing the pressure derivative in a centrifugal field in terms of radius and rearranging, the activity coefficient derivative can be found.

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P,r} = RT\left(\frac{1}{x_1} + \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P}\right) \tag*{(3-3}$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,r,x_1} = \overline{V}_1 \tag*{(3-4}$$

where $\overline{V}_1$ is the solute partial molar volume. In a centrifugal field,

$$dP = \rho\, \omega^2\, r\, dr \tag*{(3-5}$$

where ω is the angular velocity in radians per second.

$$\left(\frac{\partial \mu_1}{\partial r}\right)_{T,P,x_1} = -M_1\, \omega^2\, r \tag*{(3-6}$$

where M_1 is the solute molecular weight. Substituting equations (3-3), (3-4), (3-5) and (3-6) into equation (3-2) and rearranging gives

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_T = \frac{(M_1 - \rho\, \overline{V}_1)\, \omega^2\, r}{RT}\left(\frac{dr}{dx_1}\right) - \frac{1}{x_1} \tag*{(3-7}$$

In equation (3-7) the term $(M_1 - \rho\overline{V}_1)$ is called the sedimentation parameter. It is a function only of the physical properties of the compounds used and is determined from other measurements. The angular velocity, ω, and radius are measured directly. The concentration profile dr/dx_1 is determined from the interference fringes.

High speed centrifugation has been used in the past by Cullinan and co-workers (Cullinan, 1968; Cullinan and Lenczyk, 1969; Sethy and Cullinan, 1972 and Rau, 1975) for obtaining activity coefficient data. However, they used a preparatory ultracentrifuge, requiring that the machine be stopped and samples withdrawn by syringe. Besides the possibility of causing disturbances in the distribution, this technique limited their work to mid-range concentrations where vapor-liquid equilibrium (VLE) measurements are of comparable accuracy and sensitivity. In their initial work, Cullinan and Lenczyk (1969) used the method for the system hexane-carbon tetrachloride. They assumed the sedimentation factor $(M_1 - \rho\overline{V}_1)$ remained constant over the range of hexane compositions (35% to 65%) and obtained results within 5% of those calculated from VLE (Christian et al., 1960). Later, Sethy and Cullinan (1972) and Rau (1975) used the same method on the carbon tetrachloride-acetone system. By substituting the composition derivative of the Wilson (1964) activity coefficient model into equation (3-7), centrifuge data over nearly the entire composition range were regressed to obtain Wilson (1964) parameters. Figure 3-4 shows activity coefficient derivatives of Rau's (1975) experiments on this system. They are very similar to the results obtained using the Wilson (1964) parameters reported by Prausnitz et al. (1967) indicating that the method is reliable for midrange concentrations.

The ultracentrifuge, equipped with a conventional light source such as a mercury arc lamp, has been used to measure thermodynamic properties and molecular weights of biochemicals, polymers and salt solutions (Johnson et al., 1954; Richards and Schachman, 1959; Johnson et al., 1959; Nichol and Winzor, 1976; Hwan et al., 1979; Hsu, 1981). Earlier investigators used Schlieren optics for the refractive index profile in the

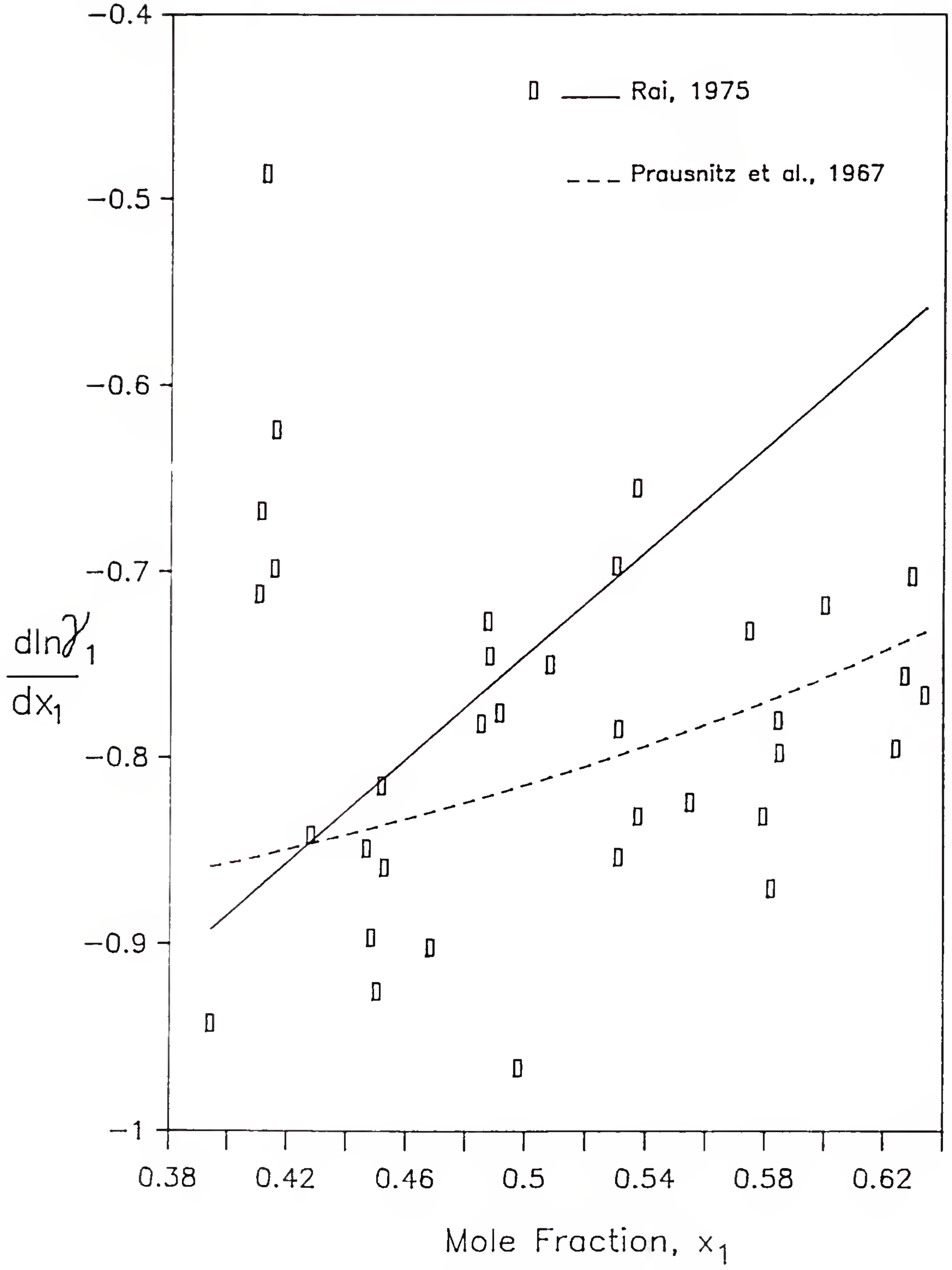

Figure 3-4 Activity Coefficient Derivative Data Calculated From the Ultracentrifuge Data of Rau (1975) For the System Carbon Tetrachloride(1) / Acetone(2). Also Shown is the Wilson Model Fit to the Ultracentrifuge Data of Rau and to VLE Data, as Given by Prausnitz (1967).

sedimented solution. More recent investigators (Richards and Schachman, 1959; Johnson et al., 1959) point out that Rayleigh interference optics is more accurate for equilibrium sedimentation experiments. Conventional light is not coherent enough to give an interference pattern with the non-electrolyte, low molecular weight organic systems of interest here. Williams (1972; 1978) describes a laser light source which yields Rayleigh interference patterns from these systems.

Equipment

Apparatus

A Beckman Model E analytical ultracentrifuge (serial #685), modified with a laser light source, was used in the present studies. This ultracentrifuge can spin a sample at speeds from 10,000 rpm to greater than 50,000 rpm. The rotor used in these experiments was an AN-D type (serial #3581). This is an aluminum rotor with a maximum safe speed of 52,000 rpm when new. The high stress of continued operation at high speed weakens the metal in the rotor, requiring that the maximum safe operating speed be lowered with age. The sample cells were double sector (chamber) type, 12 mm deep. The aluminum cell was manufactured by Beckman and the titanium cell was custom manufactured by Central Machine Products, Gainesville, FL. The sapphire cell windows were from Adolf Meller Company, Providence, RI. The window liners were originally thin (15 mils) strips of PVC as suggested by Yphantis (Ansevin et al., 1970) to cut down on the stress distortion of the windows at high speed. However, the organic solvents studied here attacked the PVC. Therefore, teflon of approximately the same thickness was substituted. All other cell parts were standard Beckman elements. Appendix A gives more details of the cell assembly and operation of the ultracentrifuge.

The ultracentrifuge has a vacuum chamber which can be evacuated to about 1 Kpa to allow the rotor to spin with very little air resistance which would raise the rotor and sample temperature. The chamber is controlled at temperatures from 10° C to 35° C ± 0.5° C using a heating element in the bottom of the chamber and a refrigeration system. The temperature of the rotor is sensed by a thermistor in the base of the rotor. For details of the thermistor calibration, see Appendix A.

The optical system used to detect the concentration profile is shown in Figure 3-5. Its design was based on that of Williams (1972; 1978; 1985). Alignment was accomplished by combining the procedures of several authors (Rees et al., 1974; Richards et al., 1971a; 1971b; Gropper, 1964; Dyson, 1970) with helpful suggestions of Williams (1985). The resulting alignment procedure is given in Appendix B. In short, the optics consist of a Spectra-Physics 5 milliwatt HeNe laser (Model 105-1) mounted on the ultracentrifuge frame. The laser light is expanded with a spatial filter and passes through the rotating sample, just as conventional light would. The interference pattern between the solution side of the cell and the pure solvent (reference) side is established using a Rayleigh interference mask.

The fringe pattern was exposed on a strip of Technical Pan 2415, Estar-AH based Kodak film held in place with a custom made film holder and developed using standard darkroom techniques with Kodak D-76 developer and Kodak fixer. The radial location of each shifted fringe is then determined with a Nikon Shadowgraph, Model 6C (#7244) microcomparator. Two reference marks on the image, whose radial locations are known exactly, yield the actual radial distance to each shifted fringe.

Composition Detection

From the photographic negative (illustrated in Figures 3-6 and 3-7) the composition profile in the cell at equilibrium is determined. Each fringe, j, along the radius, r, that is shifted from the horizontal is equivalent to a constant refractive index change, Δn.

$$j(r) = \Delta n \, d/\lambda \qquad (3\text{-}8$$

where d is the cell depth and λ is the light wavelength, 632.8 nm.

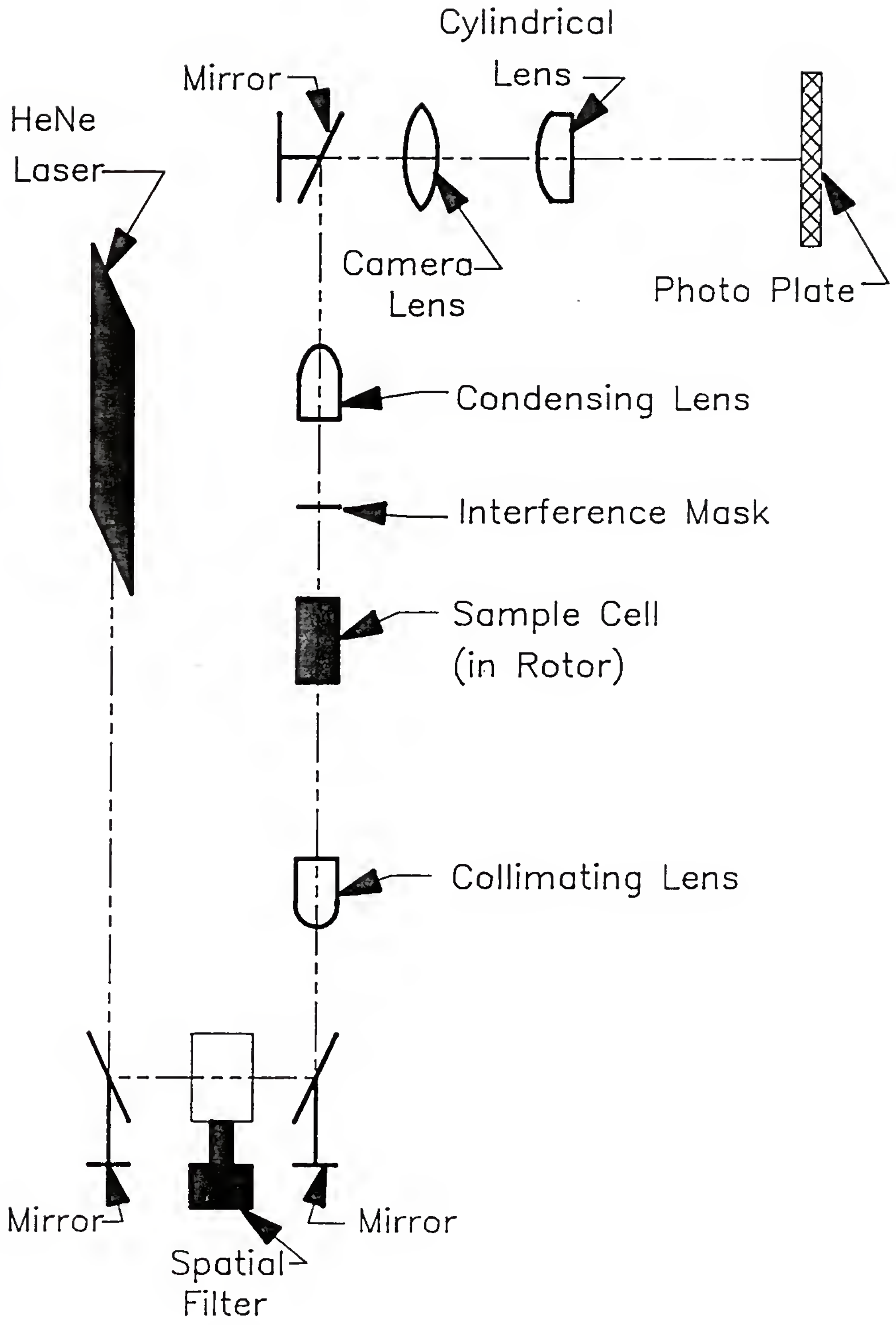

Figure 3-5 Schematic of the Laser Optics Used in the Ultracentrifuge for Composition Detection.

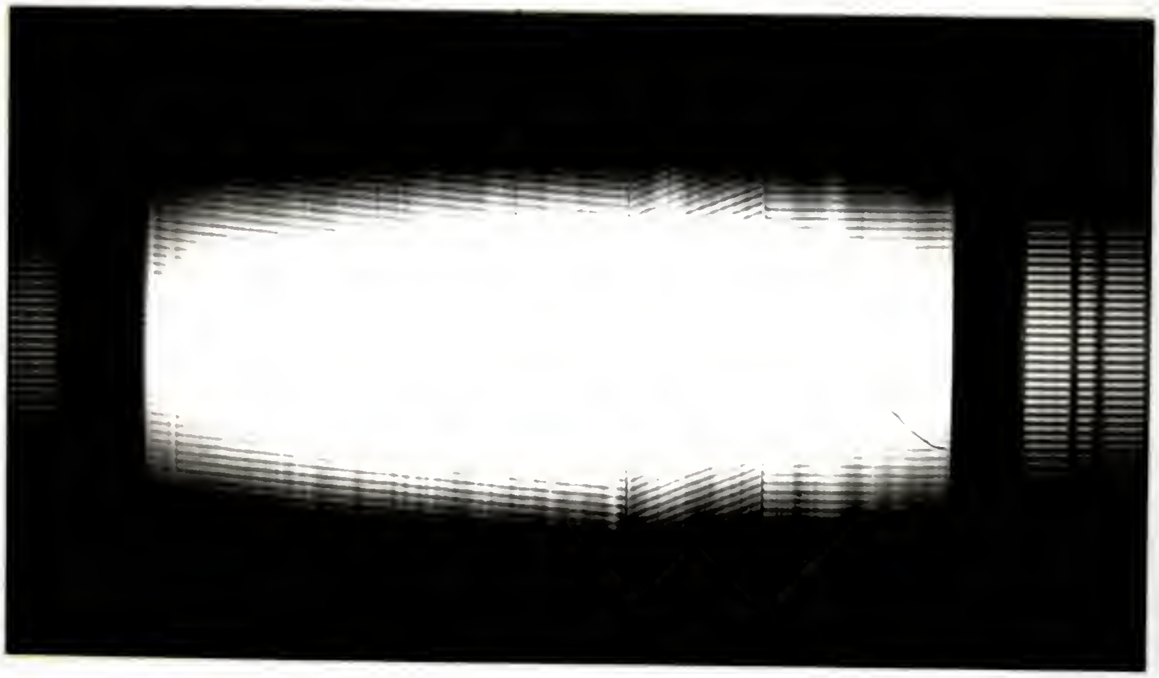

Figure 3-6 Laser Light Fringe Photo From the Ultracentrifuge, Showing a Sample of Carbon Disulfide / Acetone. The Initial Concentration of Carbon Disulfide was 3.56% (Mole) and the Speed of Rotation was 21739 RPM.

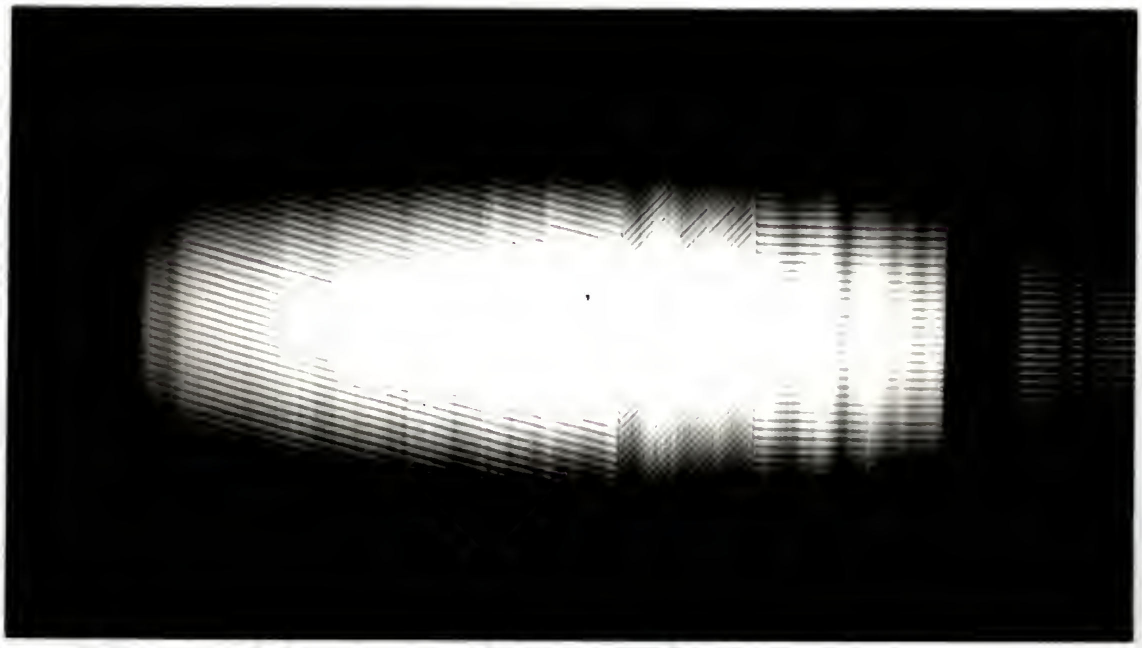

Figure 3-7 Laser Light Fringe Photo From the Ultracentrifuge, Showing a Sample of Carbon Disulfide / Acetone. The Initial Concentration of Carbon Disulfide was 3.56% (Mole) and the Speed of Rotation was 37000 RPM.

By measuring the horizontal distance between each of the fringes, a relative refractive index can be determined as a function of position, r. Because the concentration at the surface is finite, the actual refractive index profile and the concentration profile must be determined by material balance. By separately measuring the refractive index as a function of solute mole fraction, $n(x_1)$, and knowing the initial mole fraction, x_1^o, and volume of the cell, ν, the actual composition profile, $x_1(r)$, can be determined. The following equations give the conversion from fringes to composition profile:

$$\int_{r_b}^{r_t} w(r)\ d\ x_1[n(r)]\ \rho[x_1(r)]\ dr = \nu\ \rho^o\ x_1^o \qquad \text{(3-9}$$

where ρ^o is the solution density at x_1^o, $w(r)$ is the cell width normal to the radius which varies with radius in the cells used, and $\rho[x_1(r)]$ is the solution density at the position, r, with solute mole fraction $x_1(r)$:

$$n(r) = j(r)\ \lambda\ /\ d + n' \qquad \text{(3-10}$$

where n' is the refractive index at the top of the sample, at $j=0$. Equations (3-9) and (3-10) are used to iteratively solve for the unknown n'. Then, equation (3-10) gives the full composition profile in the cell. The analysis starting with the microcomparator measurements at each fringe and leading to $x_1(r)$ are carried out with the FORTRAN computer program FRNGCNV. This program is listed in Appendix C. It is fully documented with comments and a sample input and output file.

While the program has the capability of approximating the mixture refractive index from pure component values with several mixing rules, all final calculations used new refractometer data fitted to a linear equation. These were carried out in a Cromatix differential refractometer (Milton Roy Corporation, Model KMX-16). The refractometer measures the difference between a solution of known composition and the pure solvent. The light source is a HeNe laser of the same wavelength as that on the ultracentrifuge eliminating any effect of wavelength on the refractive index. The refractometer was first calibrated with known solutions of dried, reagent-grade sodium chloride and deionized water using the data at 25° C of Kuis (1936).

Refractive index measurements were made on all systems used in the ultracentrifuge in the range 0-10 mole percent solute. For carbon disulfide-acetone, literature data from Campbell and Kartzmark (1973) and Loiseleur et al. (1967) exists. The experimental data measured here compare favorably with the literature data. All refractive index data were fitted to a first or second order polynomial in x_1. The data and expressions are given in the next chapter.

Once the composition profile is found, equation (3-11), which is a finite difference approximation to equation (3-7), can be used directly, with the necessary physical properties, to calculate the desired activity coefficient derivative.

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,r=r_j} = \frac{(M_1 - \rho\, \overline{V}_1)\, \omega^2\, (r_j^2 - r_{j-1}^2)}{2RT\, ((x_1)_j - (x_1)_{j-1})} - \frac{1}{(x_1)_j} \qquad \text{(3-11}$$

This calculation was carried out in a Lotus 123 spreadsheet. Details of the density calculations required are given in Appendix D.

The initial speed for operation of the ultracentrifuge was estimated as described in Appendix E so that about 15 total fringes would appear. In all cases each concentration was run at two speeds to check for consistency. The first speed was based on this estimate while the second speed was either 1.5 times greater or less than the initial speed, depending on the actual number of fringes found.

System Selection

There are three major criteria to determine if a binary pair of chemicals could be suitable for study by equilibrium sedimentation. First, because of the laser light composition profile determination, an appropriate difference in refractive index must exist between the two chemicals. Second, the sedimentation parameter $(M_1 - \rho\overline{V}_1)$ must be large enough for the solute to sediment at a detectable level in the solvent under an accessible centrifugal force. Mixture density data must be available to determine this accurately. Finally, the system should be at least moderately non-ideal. That is, the dilute activity coefficient derivative should be sufficiently large that the result from equation (3-11) yields a significant difference of the two large numbers. Additional considerations are to have components of low volatility and toxicity. Here, no compounds were chosen that have a normal boiling point below 49°C.

Measuring fringe separation with the microcomparator indicated that 10 to 20 shifted fringes can be accurately found in a reasonable amount of time. This, together with the range of rotational speed, gives the limits of pure component refractive index difference and sedimentation parameter. A binary pair must have a pure component refractive index difference of at least 0.06, and a sedimentation parameter of at least 35 (measured at a solute concentration of 2%). Finally, an infinite dilution activity coefficient greater than 2, or less than 1/2 insures that the system is non-ideal enough.

The system carbon disulfide in acetone was studied because it is highly non-ideal and had been thoroughly examined by Campanella (1984). The second system, carbon tetrachloride in acetone, was studied by Cullinan and co-workers (Sethy and Cullinan, 1972; Rau, 1975) in an ultracentrifuge, which allowed a direct comparison with their method.

Since both of the above systems showed a positive deviation from Raoult's law, chloroform in acetone was selected to demonstrate the effects of negative deviations from Raoult's law. While no sedimentation data exist for this system, there are many vapor-liquid equilibrium literature data references.

An extensive search was made to identify two additional systems for which the ultracentrifuge could supply useful dilute solution information. The following classes of systems were identified as being interesting:

1. water/nitrile
2. water/amine
3. chloroalkene, alkene or alkane/cyclic ether
4. alcohol/alkane
5. amine/chlorinated alkane
6. nitrile/alkane or cyclic alkane
7. alcohol/chlorinated alkane

These were first evaluated by refractive index differences, Δn. In the first group, water and benzonitrile were identified as the only common system with Δn > 0.06 (Δn = 0.19). However this system is only partially miscible. The candidate system water/acetonitrile had a refractive index difference of only 0.03.

For the second group, triethyl amine was selected among the lower molecular weight nonaromatic amines since refractive index generally increases with carbon number. For water/triethyl amine, Δn = 0.06. Aromatic amines give larger Δn values (e.g., for water/aniline Δn = 0.2) but these show immiscibility.

For the third group, several cyclic ethers (furan, tetrahydrofuran, pyran, tetrahydropyran and 1,4-dioxane) were considered for solution with tetrachloroethylene or trichloroethylene. However, the only pairs with a suitable refractive index difference are tetrachloroethylene with either 1,4-dioxane (Δn = 0.09) or tetrahydrofuran (Δn = 0.08). With pyran the only alkane and alkene with a large enough Δn are heptane and hexene.

The best pair from the fourth group would involve a low carbon number alcohol such as methanol, and a high carbon number alkane such as n-octane (Δn = 0.07).

For the fifth group the aliphatic amines and linear aliphatic monochlorides have very similar refractive indexes. Thus, an aromatic amine, N-methyl aniline, was chosen to be paired with chloroform (Δn = 0.12) or monochlorobutane (Δn = 0.09).

In the sixth group aliphatic nitriles and alkanes have nearly the same refractive index. However, benzonitrile can be paired with either a linear or cyclic alkane, such as with heptane $\Delta n = 0.13$ or cyclohexane $\Delta n = 0.11$. Also, the acetonitrile/benzene system has $\Delta n = 0.16$.

Finally, chloroform and carbon tetrachloride have the highest refractive index of chlorinated alkanes. Therefore, with any alcohol, particularly methanol, either of these compounds has an adequate Δn.

The systems above were then evaluated by their ability to sediment as measured by their sedimentation parameter. For screening purposes, the factor $(M_1 - \rho\overline{V}_1)$ was approximated by $(M_1 - \rho_{0.02}V_1^o)$ where the density $(\rho_{0.02})$ was for a solute concentration of 2% (mole).

Table 3-1

Sedimentation Factors For Various Binary Pairs

Binary Pair	Sedimentation Factor $(M_1 - \rho_{0.02}V_1^o)$
water/benzonitrile	0
water/triethyl amine	5
water/aniline	0
tetrachloroethylene/1,4-dioxane	59
tetrachloroethylene/tetrahydrofuran	38
methanol/n-octane	4
chloroform/methyl aniline	39
N-methyl aniline/chlorobutane	0.5
benzonitrile/heptane	30
benzonitrile/cyclohexane	20
benzene/acetonitrile	36
chloroform/methanol	55
carbon tetrachloride/methanol	75
chloroform/acetone	54
carbondisulfide/acetone	27
carbon tetrachloride/acetone	75

From the table above it is easily seen that the sedimentation parameter is less than the desired 35 for many of the candidate systems. The only systems, not previously selected, with a high enough sedimentation factor were tetrachloroethylene with either 1,4-dioxane or tetrahydrofuran, N-methyl aniline with chloroform (or carbon tetrachloride), chloroform (or carbon tetrachloride) with methanol and benzene with acetonitrile. Final selection of benzene with acetonitrile and methanol with carbon tetrachloride was based on low toxicity, and availability of solution densities and compressibilities.

Error Analysis

Equation (3-7) describes the fundamental relationship between the derivative of the activity coefficient and measurements in the ultracentrifuge. All quantities in that equation except the derivative dr/dx_1 are well defined as to their expected uncertainty. This derivative must be calculated by an iterative integral method. For that reason the analysis of error for this process is done in two steps. First, the effect of variations in dr/dx_1 on the activity coefficient derivative is found. Then the error to be expected in the dr/dx_1 term is determined.

An uncertainty analysis (Holman, 1971) can determine the uncertainty in the activity coefficient derivative. This method assumes that a quantity in question, A, can be written in terms of several independent variables, a_i.

$$A = A(a_1, a_2, a_3, \ldots . a_n) \qquad (3\text{-}12$$

If each variable a_i has an uncertainty U_i, the uncertainty in A, U_A can be written as

$$U_A = \left[\left(\left(\frac{\partial A}{\partial a_1} \right) U_1 \right)^2 + \left(\left(\frac{\partial A}{\partial a_2} \right) U_2 \right)^2 + \ldots . + \left(\left(\frac{\partial A}{\partial a_n} \right) U_n \right)^2 \right]^{1/2} \qquad (3\text{-}13$$

In equation (3-7) the variables of interest are ρ, $\overline{V}_1$, ω, r, T, x_1^o. If the activity coefficient derivative is defined as A and (dr/dx_1) as D, equation (3-7) becomes

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_T = A = \frac{(M_1 - \rho\, \overline{V}_1)\, \omega^2\, r}{RT}\, D - \frac{1}{x_1} \qquad (3\text{-}14$$

and equation (3-13) can be written for this specific case as

$$U_A = \left[\left(\left(\frac{\partial A}{\partial \rho} \right) U_\rho \right)^2 + \left(\left(\frac{\partial A}{\partial \overline{V}_1} \right) U_{\overline{V}_1} \right)^2 + \left(\left(\frac{\partial A}{\partial \omega} \right) U_\omega \right)^2 + \left(\left(\frac{\partial A}{\partial r} \right) U_r \right)^2 + \left(\left(\frac{\partial A}{\partial T} \right) U_T \right)^2 + \left(\left(\frac{\partial A}{\partial x_1^o} \right) U_{x_1^o} \right)^2 + \left(\left(\frac{\partial A}{\partial D} \right) U_D \right)^2 \right]^{1/2} \qquad \text{(3-15}$$

The measurement of refractive index as a function of composition was done in an instrument of much greater accuracy than required for the ultracentrifuge experiment. Thus, the uncertainty in this quantity is ignored. Each of the derivatives in equation (3-15) can be evaluated from equation (3-14) and substituted into equation (3-15) giving

$$U_A = \left[\left(\frac{\overline{V}_1 \, \omega^2 \, r}{RT} \; D \; U_\rho \right)^2 + \left(\frac{\rho \, \omega^2 \, r}{RT} \; D \; U_{\overline{V}_1} \right)^2 + \left(\frac{2 \, (M_1 - \rho \overline{V}_1) \, r \, \omega}{RT} \; D \; U_\omega \right)^2 + \left(\frac{(M_1 - \rho \overline{V}_1) \, \omega^2}{RT} \; D \; U_r \right)^2 + \left(\frac{(M_1 - \rho \overline{V}_1) \, r \, \omega^2}{RT^2} \; D \; U_T \right)^2 + \left(\frac{1}{(x_1^o)^2} D \; U_{x_1^o} \right)^2 + \left(\frac{(M_1 - \rho \overline{V}_1) \, r \, \omega^2}{RT} \; U_D \right)^2 \right]^{1/2} \qquad \text{(3-16}$$

Uncertainties were assigned to each of the quantities in question as follows:

$U_\rho = 0.1\%$ $\qquad U_{\overline{V}_1} = 0.1\%$

$U_T = 0.5$ C° $\qquad U_{x_1^o} = 0.0002$

$U_\omega = 0.1\%$ $\qquad U_r = 0.001$ cm

Typical values (from run 38-2 $x_1^o = 0.035$ and run 29-1, $x_1^o = 0.109$) were substituted into equation (3-16) to illustrate the relationship of the uncertainty in D (dr/dx_1) to uncertainties in A $\left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)$. The results are shown in Table 3-2.

Table 3-2

Uncertainty in $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$ as a function of

the Uncertainty in $\left(\frac{dr}{dx_1}\right)$

	$x_1^o = 0.035$		$x_1^o = 0.109$	
$U_D^{\dagger}$ %	$U_A^{\ddagger}$	$U_A^{\ddagger}$ %	$U_A^{\ddagger}$	$U_A^{\ddagger}$ %
0.1	0.2	3.5	.02	0.3
1.0	0.3	5.5	.05	1.0
5.0	1.0	20.8	.23	4.5

† % Uncertainty in $\left(\frac{dr}{dx_1}\right)$

‡ Absolute and % Uncertainty in $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$

The error to be expected in (dr/dx_1) will now be examined by introducing a random error into its primary variables, x_1, j and r. This error will be of an average magnitude to be expected in the experiment. As an example, the fringe measurements from run 38-2 (carbon disulfide/acetone) were used. The average error in r, as indicated above, should be no more than 0.001 cm, but a worst case of 0.01 cm is used here. Then the measurements on run 38-2, which has only 8.9 fringes, would have an error of about 0.1 fringes. A summary of the contribution of various errors in the experimental quantity (dr/dx_1) and subsequently $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$ is given in Table 3-3 for the most severe case ($x_1^o = 0.035$).

Table 3-3

Errors in $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$ and $\left(\frac{dr}{dx_1}\right)$

$x_1^o = 0.035$

Cause of Error	$U\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$U\left(\frac{dr}{dx_1}\right)$
radius	5.5%	1%
j (fringes)	6.5%	1.3%
x_1^o initial solute mole frac.	3.5%	0.1%

The error due to radius measurement and fringe number are redundant, since they are absorbed in the same effect, the number of fringes. The error introduced in x_1^o could be added to the other, yielding for a total maximum error in $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$ of less than 10% at low concentrations.

Summary

Direct measurements of the dilute solution activity coefficient derivative would be valuable to settle discrepancies between extrapolated vapor-liquid equilibrium measurements and direct measurements of infinite dilution activity coefficients, for differences between activity coefficient models and for theoretical and modeling purposes. The analytical ultracentrifuge has the capability of providing these.

The experimental equipment, including the laser light source for sensitive Rayleigh Interference composition measurement, have been described. A complete thermodynamic analysis of the ultracentrifuge has been given for the solute activity coefficient derivative in terms of the measurable quantities in the ultracentrifuge. A complete uncertainty analysis was conducted for the experiment. It pointed out that with reasonable care the activity coefficient derivative can be determined to within 10% at concentrations near 2%.

Not all binary systems of chemicals are amenable to this technique. There must be a moderate difference in refractive index of the pure components ($\Delta n > 0.06$), a sufficient tendency of the solute to sediment in the solvent, $[(M_1 - \rho\overline{V}_1) > 35]$ and moderate non-ideality ($\gamma_1^{\infty} > 2$) so that the activity coefficient derivative is large enough to be well determined. A thorough screening was conducted to select interesting systems to meet these criteria. Five systems were chosen and both sedimentation and refractive index measurements were made on them.

CHAPTER 4

EXPERIMENTAL MEASUREMENTS OF DILUTE SOLUTION ACTIVITY COEFFICIENT DERIVATIVES

Introduction

Experimental measurements were made to obtain the composition derivative of the solute chemical potentials and activity coefficients of five systems: carbon disulfide in acetone, carbon tetrachloride in acetone, chloroform in acetone, benzene in acetonitrile, and carbon tetrachloride in methanol. Experiments were conducted on all systems over a range of composition, usually from 1.5% (mole) to 10% (mole) in the solute (first component listed). Tests were usually conducted at three temperatures, 10°, 25° and 35° C.

Equation (4-1) shows the basic relationship between the activity coefficient derivative and experimentally accessible quantities

$$\left(\frac{\partial\mu_1/RT}{\partial x_1}\right) = \left(\frac{\partial \ln\gamma_1}{\partial x_1}\right) + \frac{1}{x_1} = \frac{(M_1 - \rho\overline{V}_1)\,\omega^2\, r}{RT}\left(\frac{dn}{dx_1}\right)\left(\frac{dr}{dn}\right) \qquad \text{(4-1}$$

The density, ρ, and partial molar volume, $\overline{V}_1$, are obtained from literature data, the refractive index/composition derivative (dn/dx_1) was measured with a laser differential refractometer as described in Chapter 3, and the refractive index profile, (dr/dn), was obtained from the ultracentrifuge.

This chapter describes the experiments performed and presents the specific results on each system. Comparisons with analyses from vapor-liquid equilibrium (VLE) data are also made. Discussions of the influence of pressure due to cell loading and composition and of impurities are given. Tables giving detailed results for each experimental run are in Appendix F. These tables give the composition profile at each fringe, all physical properties needed and the calculated activity coefficient derivatives and chemical potential derivatives.

Carbon Disulfide/Acetone System

The carbon disulfide/acetone system was the initial system studied. As experience was gained, inconsistent results were found for some of the measurements; these were omitted. The final 21 runs adopted covered a range of carbon disulfide concentrations from 1.05% (mole) to 10.9% (mole). All concentrations were run at more than one speed to verify results. Two concentrations (10.9% and 2.07%) were run at 10°, 25° and 30° or 33° C. All other runs were at 25° C or 26.5° C.

A summary of the results for this system is in Table 4-1. Included are the overall solute concentration, temperature, calculated activity coefficient derivative and calculated chemical potential derivative. Also included are the activity coefficient derivatives and chemical potential derivatives calculated from parameters fitted by Gmehling et al. (1977) to the VLE data of Litvinov (1952) at 25° C for the Wilson (1964) and NRTL (Renon and Prausnitz, 1968) excess free energy models. Excess enthalpy data of Campbell et al. (1970) were used in equation (4-2) to calculate the activity coefficient at 35° C from the 25° C VLE data of Litvinov (1952).

$$(\ln\gamma_1)_{T=T_2} = \frac{\overline{h}_1^E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + (\ln\gamma_1)_{T=T_1} \qquad \text{(4-2}$$

Numerical composition derivatives of $\ln\gamma_1$ were then calculated to verify the consistency of the activity coefficient derivatives obtain from VLE data at different temperatures contained in Table 4-1. The excess enthalpy data were compiled and regressed by Gmehling et al. (1977). The chemical potential derivatives from the centrifuge experiment and from the VLE are given in Figure 4-1.

Table 4-1
Summary of Carbon Disulfide(1)/Acetone(2)
Ultracentrifuge Experimental Results
and Comparison Values Calculated from Literature VLE Data

x_1^o	T °C	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Expt+	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Expt	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Wlsn†	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ NRTL†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ NRTL†	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn‡
0.01051	25	-19.0±3.0•	74.6	-2.466	92.73	-1.828	93.36	-2.599
0.01876	26.5	-16.8±1.2	36.0	-2.440	50.87	-1.825	51.48	-2.567
0.01876	26.5	-17.4±2.1	35.5					
0.02074	10	-12.2±1.4	35.5	-2.433	45.78	-1.824	46.39	-2.560
0.02074	25	-13.5±1.9•	34.2					
0.02074	25	-8.9±3.8•	38.9					
0.02074	30	-15.2±1.8	32.5					
0.02846	18.8	-7.1±1.2	27.7	-2.409	32.72	-1.821	33.31	-2.532
0.02846	26.5	-7.0±1.1•	27.9					
0.03558	26.5	-9.9±0.7	18.1	-2.387	25.71	-1.818	26.28	-2.506
0.03558	26.5	-9.5±0.5	18.5					
0.03558	26.5	-9.5±0.7	18.4					
0.03558	26.5	-9.4±0.9	18.5					
0.03767	25	-9.9±0.8	16.4	-2.380	24.16	-1.817	24.73	-2.499
0.03767	25	-7.7±2.4•	18.7					
0.05806	26.5	-6.6±0.3	10.6	-2.319	14.90	-1.810	15.41	-2.427
0.05806	26.5	-6.7±0.3	10.4					
0.10949	10	-3.6±0.2	5.5	-2.174	6.96	-1.792	7.34	-2.261
0.10949	25	-4.7±0.1	4.4					
0.10949	25	-4.4±0.1	4.7					
0.10949	33	-3.5±0.2	5.6					

+ Standard deviations from various fringes.
† Calculated from VLE data of Litvinov (1952) at 25° C.
‡ Calculated from VLE data of Zawidzki (1900) at 35° C.
• Appear inconsistant.

The results of the ultracentrifuge experiment are numerically different from the VLE curve, though they have the same general trend with composition. Except for five runs, a factor of 1.4 times the ultracentrifuge derivatives would make them essentially coincide with the VLE values, as shown in Figure 4-1. .

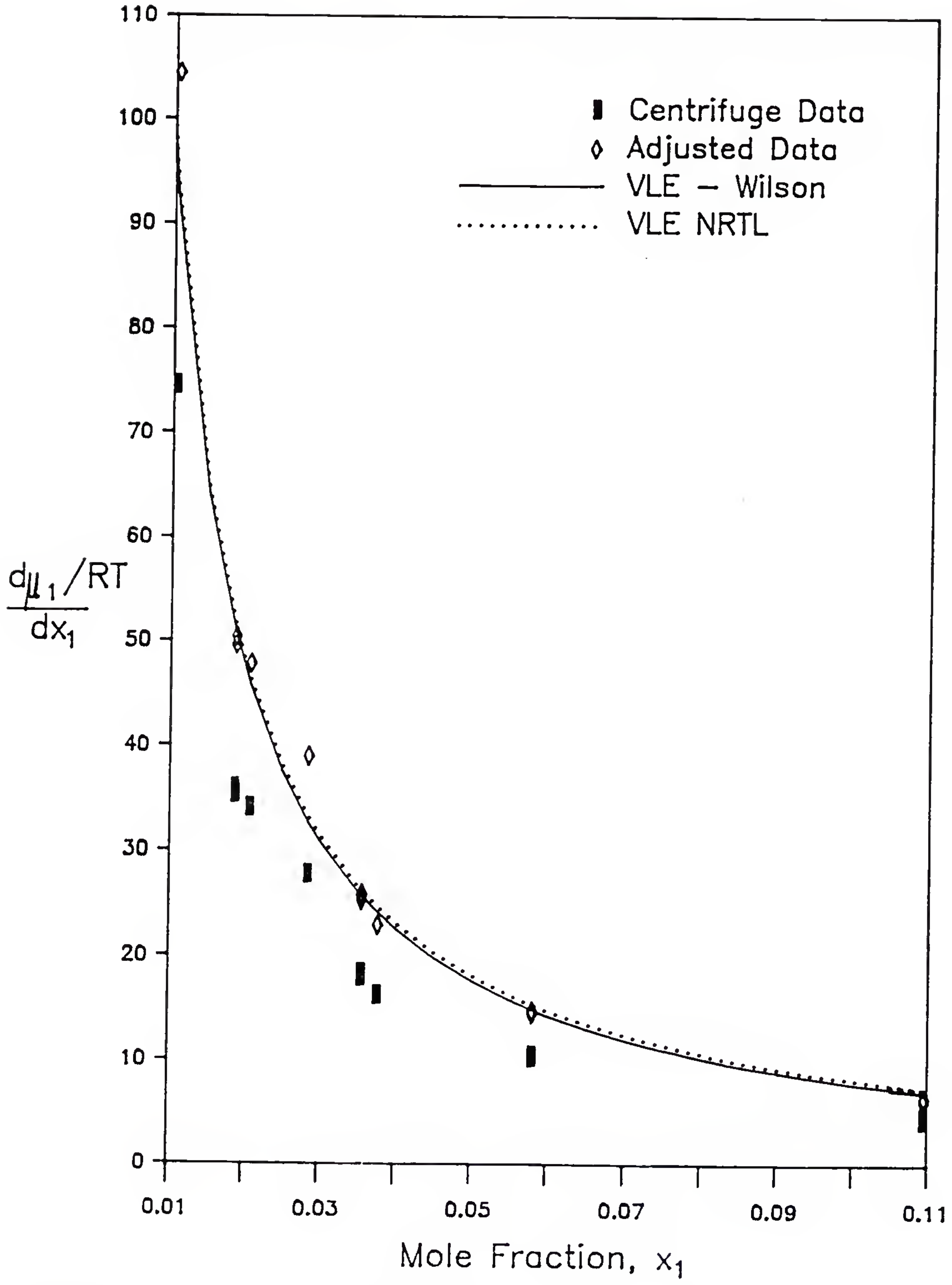

Figure 4-1 Chemical Potential Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Litvinov, 1952, at 25° C) Fitted to the Wilson and NRTL Models, for the System Carbon Disulfide(1) / Acetone(2).

Figure 4-2 shows derivatives of the activity coefficient. The filled rectangles are calculated from the ultracentrifuge experiment, the lines are from various models fitted to VLE data and the open diamonds are corrected centrifuge values. Again, it is clear that, except for five points, the corrected data are within experimental error of the calculations.

The five points that show the greatest deviation from the others and from the VLE curve are probably in error. In one the concentration of solute was only 1.05% (mole) and there was a blur in the interference pattern at the bottom of the cell. This interrupted the fringe measurements and required extrapolation to determine the total number of fringes present. Another was an early experiment for which all systems were not necessarily operating properly. The others had less than the desired number of fringes (7 to 20).

The two sets of measurements that were made at different temperatures do not show a consistent change with temperature. The values at 2.1% (mole) marginally indicate more negative activity coefficient derivatives as temperature increases, for the 10.9% (mole) system, the results at temperatures above and below do not encompass the 25° C value. Excess enthalpy and VLE data agree with the 2.1% (mole) data, indicating a slightly more negative activity coefficient derivative at higher temperatures.

It should be pointed out that refractive index/composition data have previously been measured (Campbell and Kartzmark, 1973 and Loiseleur et al. 1967). As shown in Figure 4-3 their results agree very well with the present measurements even though their light source was the sodium line (589.3 nm) rather than the 632.8 nm laser light used here. Thus, it appears that the refractive index measurements are reliable. Measurements of mixture refractive index were made at 30° and 35° C and extrapolated to other temperatures, as shown in Table 4-2.

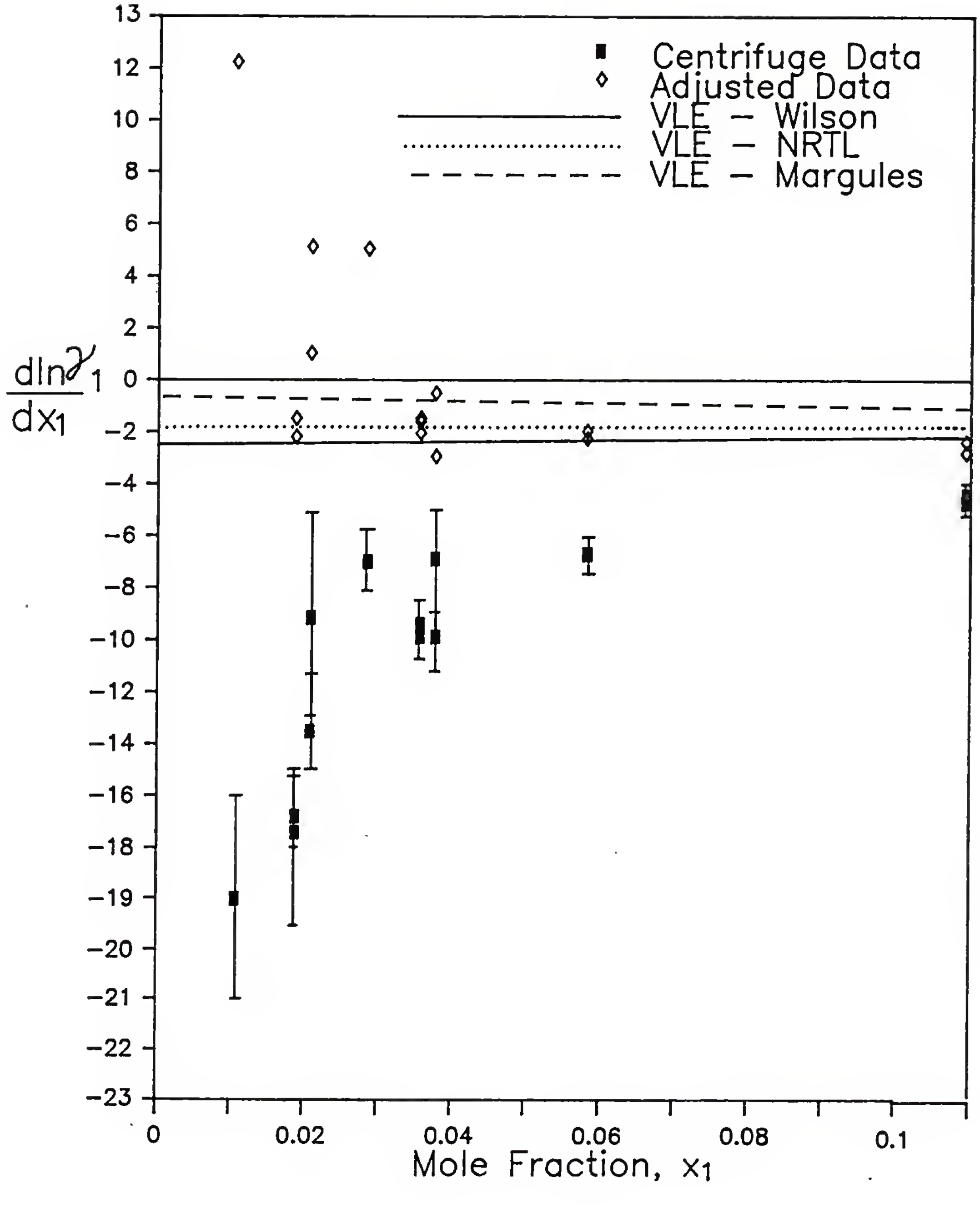

Figure 4-2 Activity Coefficient Derivatives From Ultracentrifuge Data (as Measured and Adjusted) at 25° C and From VLE Data (Litvinov, 1952, at 25° C) Fitted to Various Models, for the System Carbon Disulfide(1)/Acetone(2). Error Bars are Typical of All Ultracentrifuge Runs.

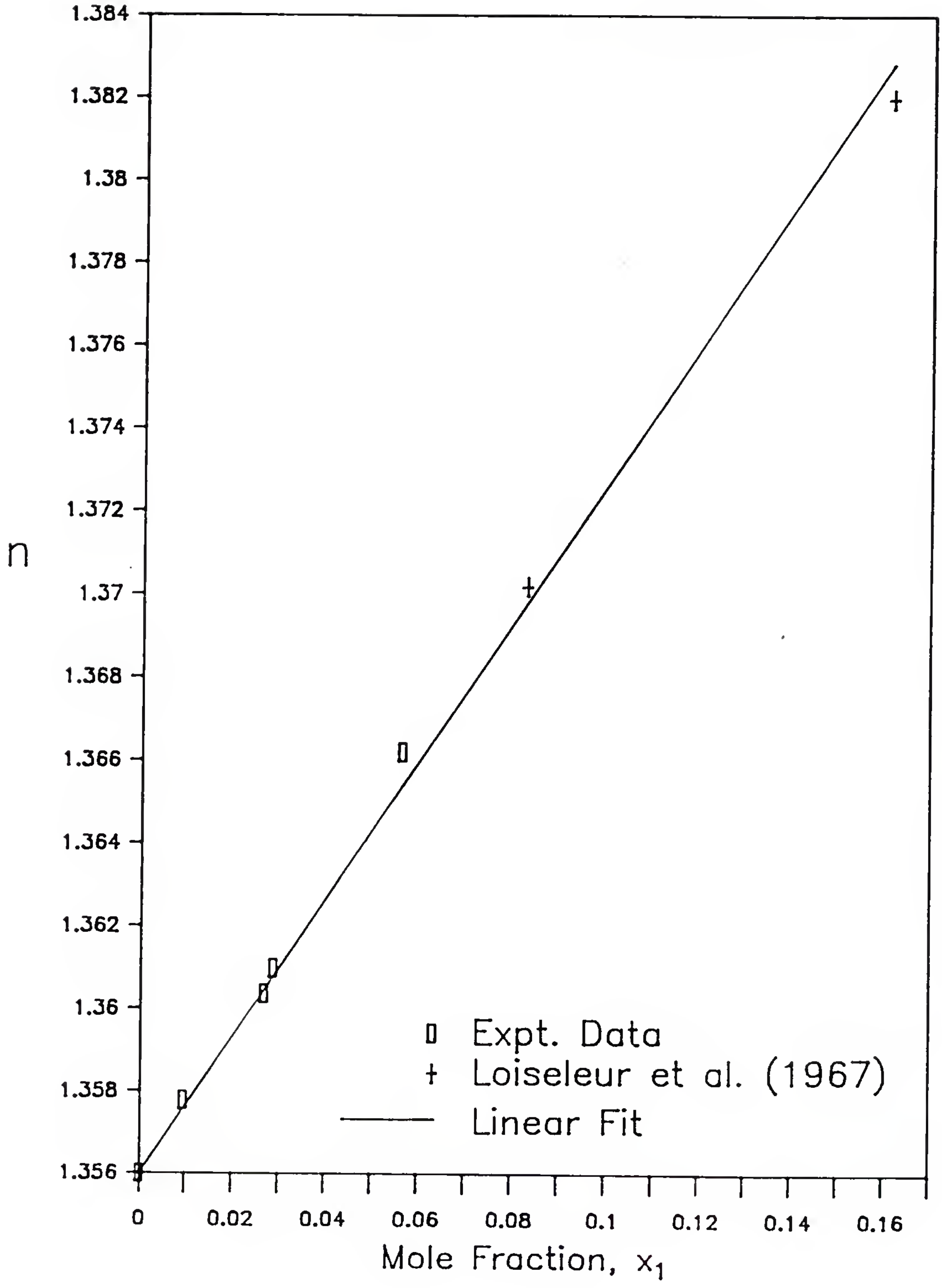

Figure 4-3 Experimental and Literature Refractive Index Data (at 25°) Fit to a Linear Equation in Mole Fraction for the System Carbon Disulfide(1) / Acetone (2).

Table 4-2
Refractive Index (n) Experimental Results
for the System Carbon Disulfide(1)/Acetone(2)

x_1	n 25° C Extrap†	n 30° C Expt	n 35° C Expt
0.00000	1.35600‡	1.35395‡	1.35183‡
0.00947	1.35786	1.35570	1.35354
0.02671	1.36045	1.35810	1.35574
0.02864	1.36106	1.35887	1.35667
0.05624	1.36629	1.36383	1.36137

† Values at 25° C were extrapolated linearly from the experimental measurements at 30° and 35° C.

‡ Pure component refractive index data was taken from Loiseleur et al. (1967) and Campbell and Kartzmark (1977).

Chloroform/Acetone System

The chloroform/acetone system is the only system examined which had negative deviations from Raoult's law. This means that the activity coefficient derivative will be positive rather than negative as in the carbon disulfide/acetone case.

A summary of the results for this system is given in Table 4-3. A range of concentrations from 1.9% (mole) to 8.7% (mole) (chloroform in acetone) was studied. Each concentration was run at two or more different speeds to verify results. At one concentration (5.3%) runs were made at both 26.5° C and 37.3° C. All other runs were made at 26.5° C. Table 4-3 also shows the activity coefficient derivatives and chemical potential derivatives calculated from the VLE measurements of Rabinovich and Nikolaev (1960) at 25° C using the Wilson, and NRTL model parameters from Gmehling et al. (1977). The higher temperature VLE data of Zawidzki (1900) given in

Table 4-3, was verified as correct by scaling the VLE data of Rabinovich and Nikolaev (1960) at 25° C to 35° C using the excess enthalpy data of Chevalier and Bares (1969).

Table 4-3
Summary of Chloroform(1)/Acetone(2)
Ultracentrifuge Experimental Results
and Comparison Values Calculated from Literature VLE Data

x_1^o	T °C	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Expt[+]	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Expt	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn[†]	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Wlsn[†]	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ NRTL[†]	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ NRTL[†]	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn[‡]
0.01888	26.5	-14.8±3.0[•]	37.2	1.720	54.69	1.569	54.54	1.221
0.01888	26.5	-15.2±2.2[•]	36.5					
0.02515	26.5	-7.8±1.2[•]	31.3	1.711	41.48	1.565	41.33	1.218
0.02515	26.5	-8.1±0.7[•]	30.9					
0.03713	26.5	-6.3±1.6	20.4	1.694	28.63	1.559	28.49	1.210
0.03713	26.5	-6.6±0.7	20					
0.03713	26.5	-6.9±2.6	19.8					
0.05269	26.5	-3.8±0.6	15	1.672	20.65	1.552	20.53	1.201
0.05269	26.5	-3.7±0.5	15.1					
0.05269	37.3	-4.4±0.6	14.4					
0.06357	26.5	-2.7±0.5	12.9	1.657	17.39	1.547	17.28	1.194
0.06357	26.5	-2.2±0.5	13.5					
0.06357	26.5	-2.7±0.6	13					
0.08724	26.5	-1.7±0.4	9.7	1.625	13.09	1.540	13.00	1.179
0.08724	26.5	-1.7±0.4	9.6					

[+] Standard deviations from various fringes.

[†] Calculated from VLE data of Rabinovich and Nikolaev (1960) at 25° C.

[‡] Calculated from VLE data of Zawidzki (1900) at 35° C.

[•] Appear inconsistant.

Figure 4-4 shows the chemical potential derivatives from the centrifuge and the VLE data. Again if all of the ultracentrifuge values are multiplied by 1.4, the results are within experimental error of those calculated from VLE data, as demonstrated in Figure 4-4. Figure 4-5 shows the derivative of the activity coefficient calculated from the ultracentrifuge experiments, from VLE data, and from the "corrected" values of

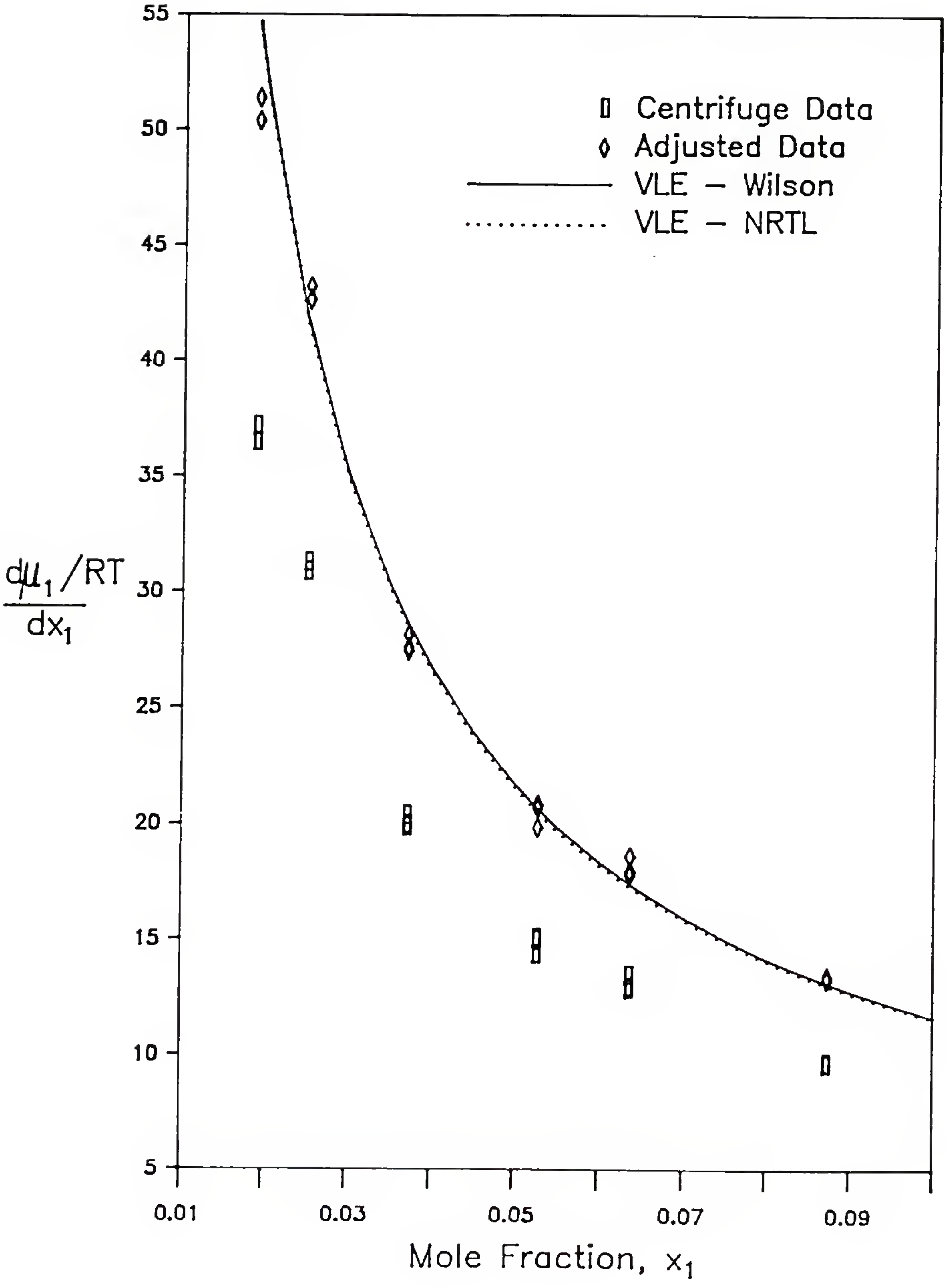

Figure 4-4 Chemical Potential Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Rabinovich and Nikolaev, 1960, at 25° C) Fitted to the Wilson and NRTL Models, for the System Chloroform(1) / Acetone(2).

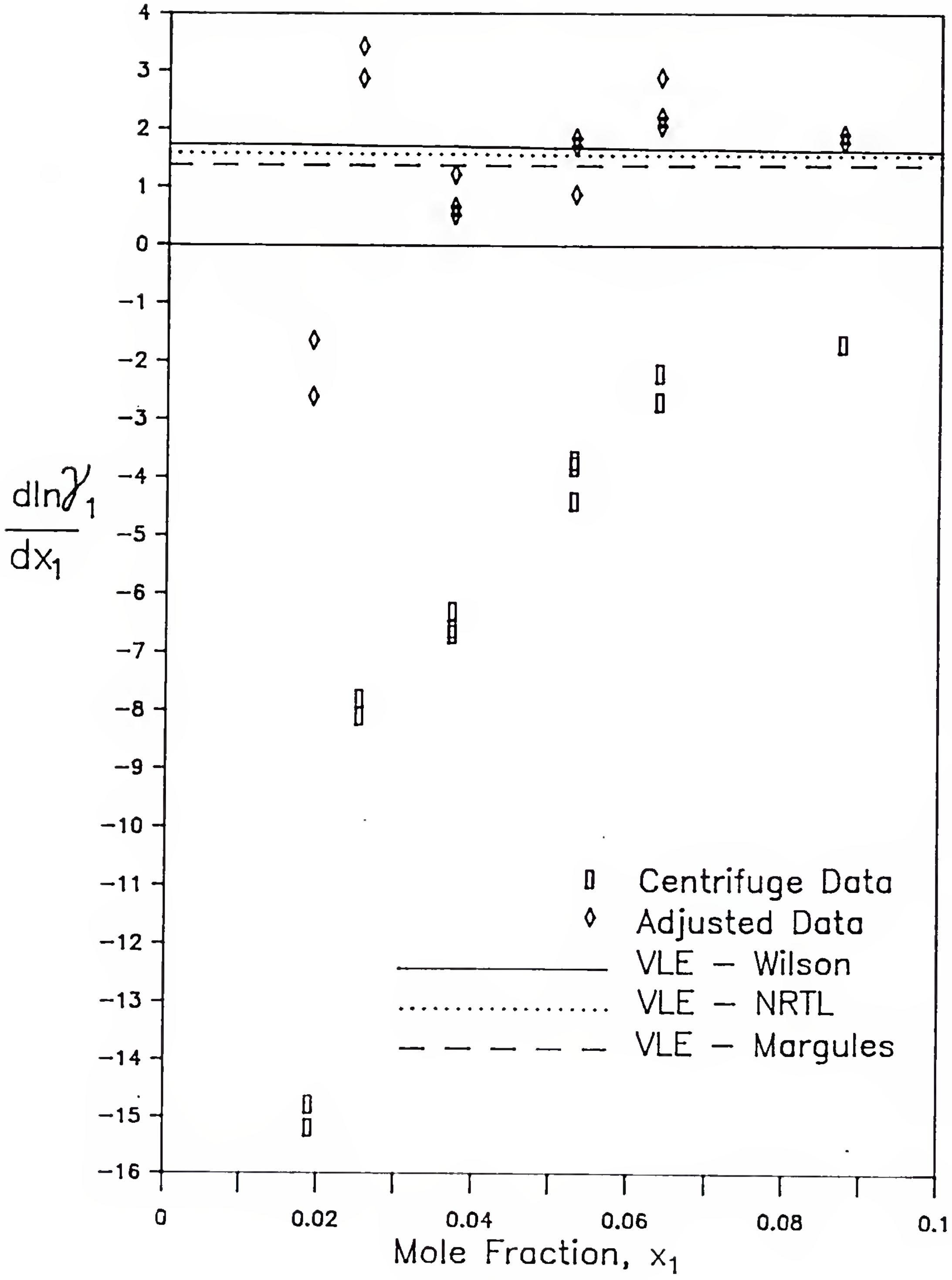

Figure 4-5 Activity Coefficient Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Rabinovich and Nikolaev, 1960, at 25° C) Fitted to Various Models, for the System Chloroform(1) / Acetone(2).

the chemical potential derivatives. It is clear that the "as measured" results are erroneous since they are negative.

One experiment (mole fraction chloroform was 0.053) was run at both 26.5° C and 37.3° C. Ultracentrifuge results give a lower activity coefficient derivative at 37.3° C than at 26.5° C. The VLE data at 35° C (Zawidzki, 1900) and 25° C (Rabinovich and Nikolaev, 1960) indicate the same trend. Negative excess enthalpy data of Chevalier and Bares (1969) further support this behavior. The difference in activity coefficient derivatives measured in the ultracentrifuge at 26.5° and 37.3° C is about 0.8. The VLE data indicate a difference in derivatives at 25° and 35° C of 0.6.

There were no mixture refractive index data for this system available in the literature. Pure acetone data were taken from Loiseleur et al. (1967) and Campbell and Kartzmark (1973), while mixture data were measured at 30°, the lowest temperature for reliable results, and 35° C. Values at 25° C were extrapolated and all data are summarized in Table 4-4.

Table 4-4
Refractive Index (n) Experimental Results
for the System Chloroform(1)/Acetone(2)

x_1	n 25° C Extrap†	n 30° C Expt	n 35° C Expt
0.00000	1.35600‡	1.35395‡	1.35180‡
0.04076	1.35985	1.35779	1.35562
0.10279	1.36561	1.36350	1.36130

† Values at 25° C were extrapolated linearly from the experimental measurements at 30° and 35° C.

‡ Pure component refractive index data were taken from Loiseleur et al. (1967) and Campbell and Kartzmark (1977).

Carbon Tetrachloride/Acetone System

For the carbon tetrachloride/acetone system measurements were made at three compositions, and multiple speeds, from a low of 0.4% (mole) to a high of 7.3% (mole) carbon tetrachloride, at 23° C for the low concentration point and 26.5° C for the others. These are summarized in Table 4-5 and show the same trend as earlier experiments. Figure 4-6 shows that the chemical potential derivatives from the ultracentrifuge follow, but are consistently lower than, those calculated from the VLE data of Brown and Smith (1957), which were adjusted from 45° C using heat of mixing data from Brown and Fock (1957).

Table 4-5
Summary of Carbon Tetrachloride(1)/Acetone(2)
Ultracentrifuge Experimental Results
and Comparison Values Calculated from Literature VLE and h^E Data

x_1^o	T	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$
	°C	Expt$^+$	Expt	Wlsn†	Wlsn†	NRTL†	NRTL†	Wlsn‡
0.00429	23	-58.6±7.0$^{\bullet}$	161.2	-1.063	231.98	-0.972	232.07	-1.271
0.00429	23	-61.3±8.9$^{\bullet}$	159.7					
0.02208	10.3	-6.7±2.0	38.2	-1.055	44.23	-0.971	44.32	-1.199
0.02208	26.5	-8.7±1.6	36.1					
0.02208	26.5	-8.1±1.4	36.5					
0.07246	26.5	-2.7±1.1	11	-1.033	12.77	-0.967	12.83	-1.086
0.07246	26.5	-2.8±0.3	10.9					
0.07246	37.3	-3.2±0.8	10.5					

$^+$ Standard deviations from various fringes.

† Calculated from VLE data of Brown and Smith (1957) at 45° C.

‡ The VLE values at 45° from Brown and Smith (1957) were adjust with the excess enthalpy data of Brown and Fock (1957) to obtain a result at 25° C.

$^{\bullet}$ Appear inconsistant.

As Figure 4-6 also shows, if all of the ultracentrifuge values are multiplied by the common factor of 1.2, the results correspond to the VLE data, particularly at the higher concentration points. Figure 4-7 shows the resulting activity coefficient derivatives for these experiments.

Two experimental ultracentrifuge runs on this system were conducted at temperatures other than those shown in Figure 4-6. At a mole fraction of 0.0221

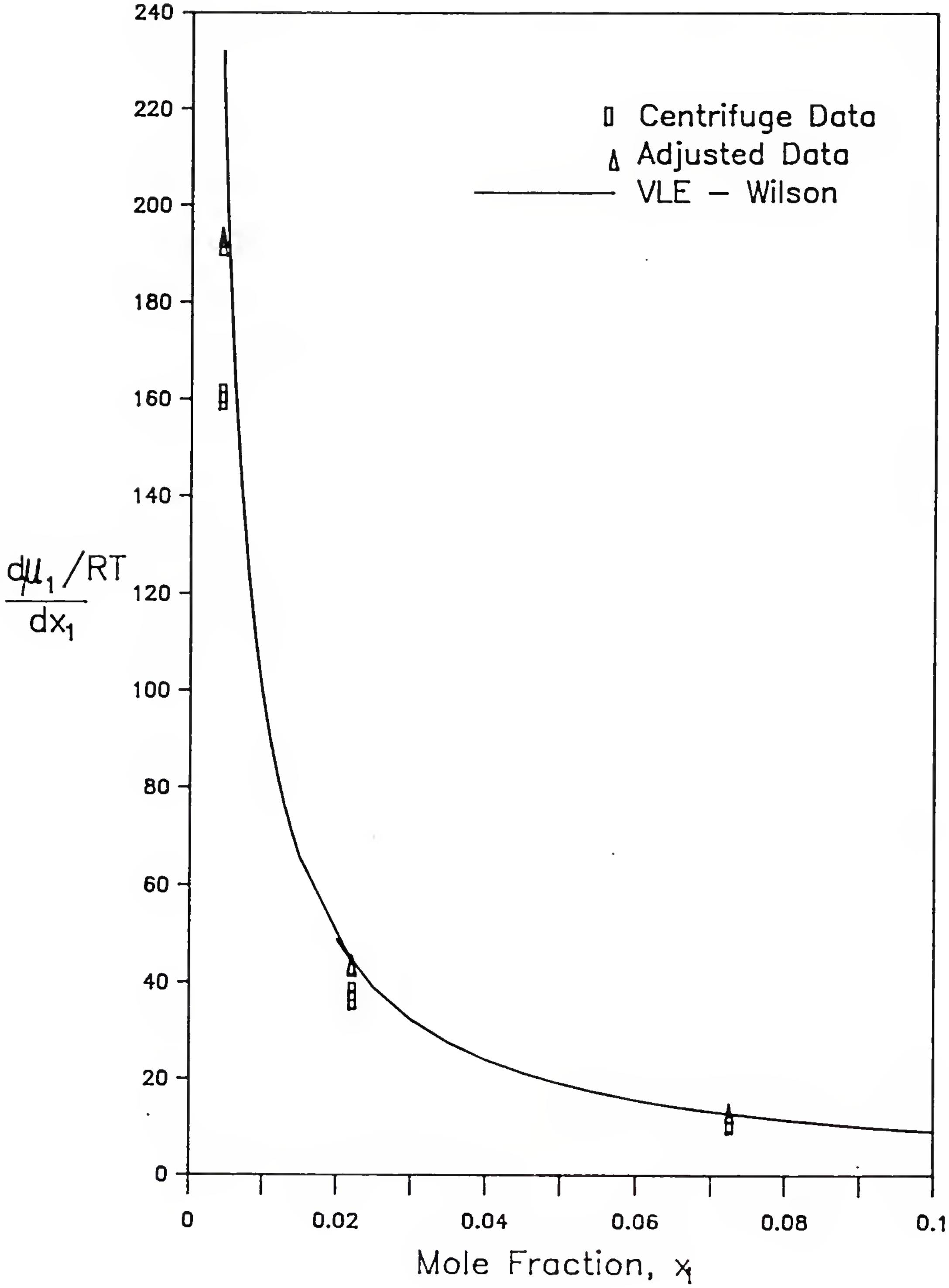

Figure 4-6 Chemical Potential Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Brown and Smith, 1957, at 45°) Fitted to the Wilson Model, for the System Carbon Tetrachloride(1) / Acetone(2).

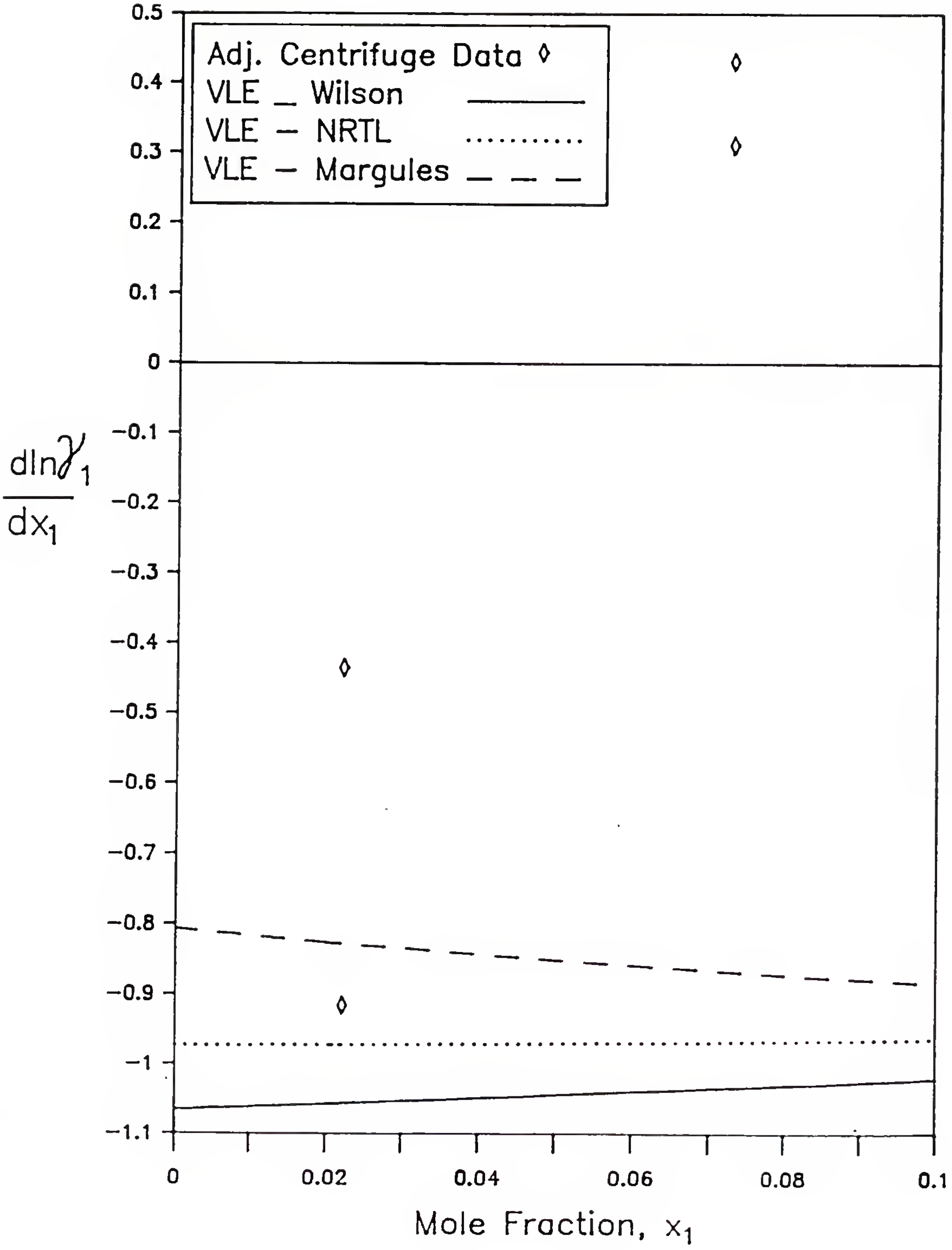

Figure 4-7 Activity Coefficient Derivatives From Ultracentrifuge Data (Adjusted) and From VLE Data (Brown and Smith, 1957, at 45°) Fitted to the Wilson Model, for the System Carbon Tetrachloride(1) / Acetone(2).

carbon tetrachloride, runs at 10° C and 26.5° C were made, while at $x_1^o = 0.0725$, runs were made at 26.5° and 37.3° C. The results showed activity coefficient derivatives that were statistically unchanged with temperature. Here the VLE and positive excess enthalpy data (Brown and Smith, 1957; Brown and Fock, 1957) give more negative derivatives with decreasing temperature.

There were no mixture refractive index data for this system available in the literature. As before, experimental mixture data were measured at 30° and 35° C and linearly extrapolated to other temperatures. This data is summarized in Table 4-6.

Table 4-6
Refractive Index (n) Experimental Results
for the System Carbon Tetrachloride(1)/Acetone(2)

x_1	n 25° C Extrap†	n 30° C Expt	n 35° C Expt
0.00000	1.35600‡	1.35395‡	1.35180‡
0.04000	1.36144	1.35930	1.35706
0.07990	1.36679	1.36459	1.36230

† Values at 25° C were extrapolated linearly from the experimental measurements at 30° and 35° C.

‡ Pure component refractive index data was taken from Loiseleur et al. (1967) and Campbell and Kartzmark (1977).

Benzene/Acetonitrile System

For the benzene/acetonitrile system, measurements were made from a low of 2.27% (mole) to a high of 8.6% (mole) benzene at 26.5° C and are summarized in Table 4-7. Again, as is shown in Figure 4-8, the chemical potential derivatives from the ultracentrifuge follow, but are consistently lower than, those calculated from the VLE data of Werner and Schuberth (1966) at 20° C (using the Wilson and NRTL equations with parameters fit by Gmehling et al. 1977).

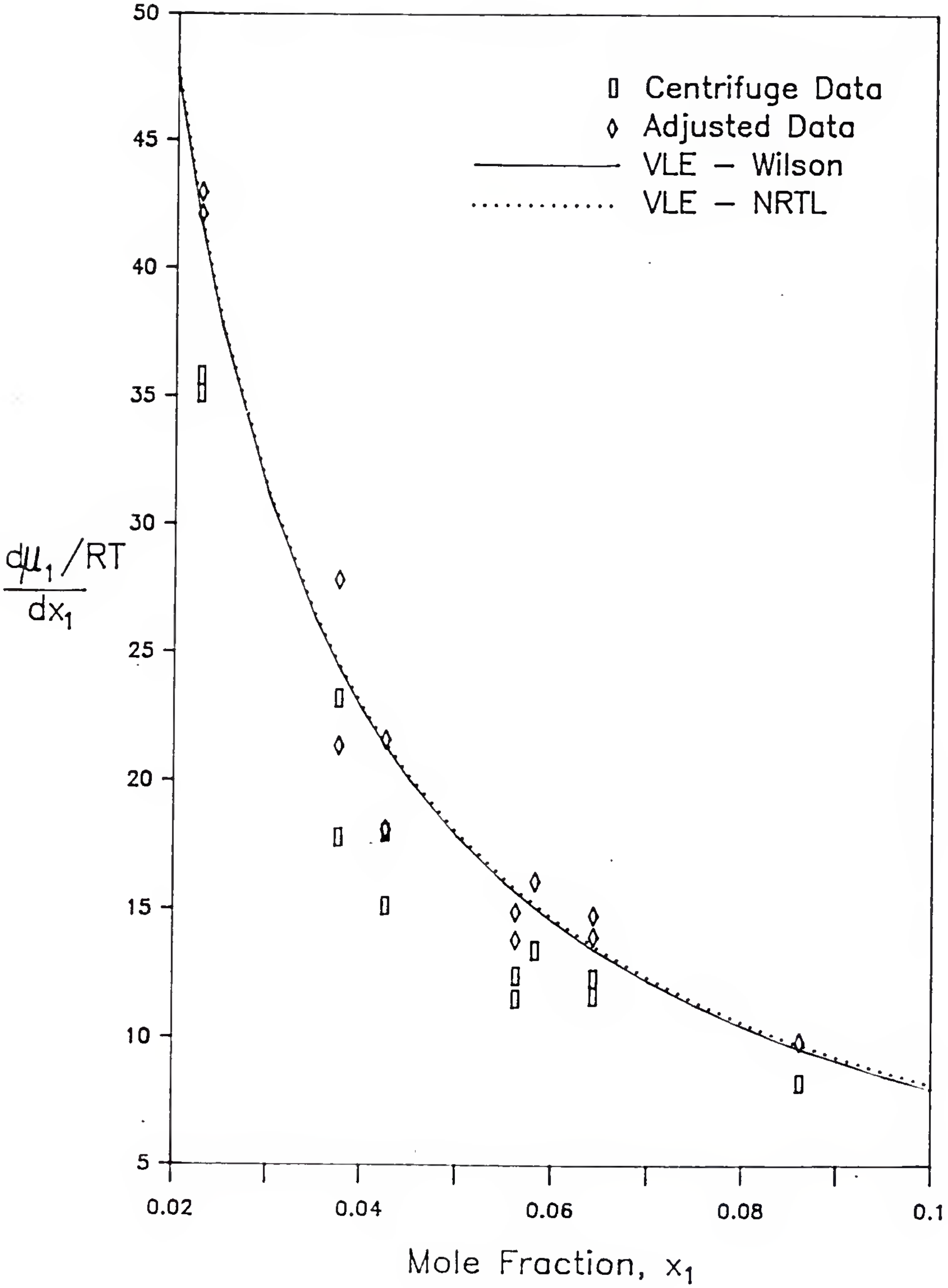

Figure 4-8 Chemical Potential Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Werner and Schuberth, 1966, at 20° C) Fitted to the Wilson and NRTL Models, for the System Benzene(1) / Acetonitrile(2).

Table 4-7
Summary of Benzene(1)/Acetonitrile(2)
Ultracentrifuge Experimental Results
and Comparison Values Calculated from Literature VLE Data

x_1^o	T °C	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Expt$^+$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Expt	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Wlsn†	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ NRTL†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ NRTL†	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn‡
0.02271	26.5	-8.6±1.1	35.1	-2.274	41.78	-2.166	41.89	-1.9973
0.02271	26.5	-8.0±2.0	35.8					
0.03747	26.5	-3.4±1.7$^{\bullet}$	23.2	-2.221	24.45	-2.097	24.57	-1.9574
0.03747	26.5	-8.8±0.5$^{\bullet}$	17.8					
0.04255	26.5	-5.4±1.3	18	-2.204	21.33	-2.074	21.46	-1.9441
0.04255	26.5	-8.3±1.1	15.1					
0.04255	37.3	-8.6±1.2	14.8					
0.05622	26.5	-6.2±0.5	11.5	-2.156	15.64	-2.015	15.78	-1.9082
0.05622	26.5	-5.3±0.5	12.4					
0.05622	37.3	-6.6±0.8	11.1					
0.05821	26.5	-3.7±2.5	13.4	-2.149	15.03	-2.006	15.18	-1.9030
0.06427	26.5	-3.9±2.1	11.6	-2.129	13.42	-1.981	13.57	-1.8873
0.06427	26.5	-3.2±0.7	12.3					
0.08610	26.5	-3.4±0.3	8.2	-2.057	9.56	-1.895	9.72	-1.8322

$^+$ Standard deviations from various fringes.

† Calculated from VLE data of Werner and Schuberth (1966) at 20° C.

‡ Calculated from VLE data of Palmer and Smith (1972) at 45° C.

$^{\bullet}$ Appear inconsistant.

Multiplying all of the ultracentrifuge values by 1.2 gives values which are within experimental error of the VLE data (Figure 4-8).

The data for this system show much more scatter than the others, because lower speeds and smaller samples yielded fewer fringes in most of the runs. These less satisfactory conditions were necessary to minimize the extra spinning force on the rotor due to the heavier mass of the titanium cell used for these chemicals. Activity coefficient derivatives calculated from the "corrected" chemical potential derivatives are given in Figure 4-9.

Two compositions of this system were studied at 37.3° C. While the uncertainty is quite high, both runs appear to give more negative activity coefficient derivatives at

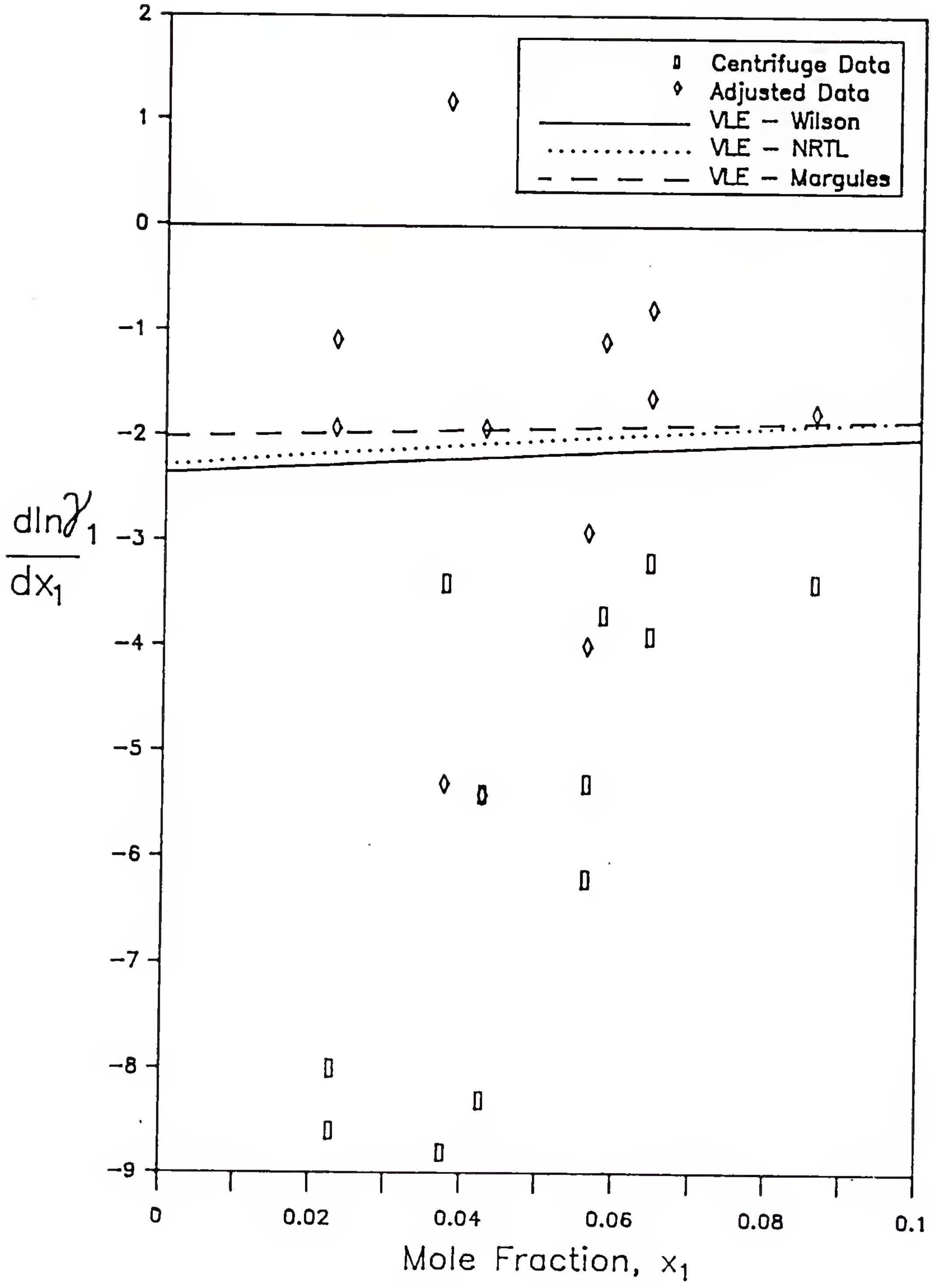

Figure 4-9 Activity Coefficient Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Werner and Schuberth, 1966, at 20° C) Fitted to Various Models, for the System Benzene(1) / Acetonitrile(2).

this higher temperature. The VLE data of Werner and Schuberth (1966) at 20° C and of Palmer and Smith (1972) at 45° C indicate a trend in the opposite direction, i.e. less negative derivative values at higher temperatures, consistent with the positive excess enthalpy of Absood et al. (1976).

There were no mixture refractive index data for this system available in the literature. The experimental data were measured at 30° and 35° C and extrapolated to other temperatures. Pure component refractive index data for acetonitrile were not available at different temperatures. The centrifuge data analysis can be done equally well with absolute or differential mixture refractive index data. Therefore, for this system, only the differential refractive index is reported in Table 4-8.

Table 4-8
Differential Refractive Index (Δn) Experimental Results for the System Benzene(1)/Acetonitrile(2)

x_1	Δn 25° C Extrap†	Δn 30° C Expt	Δn 35° C Expt
0.00000	0.00000	0.00000	0.00000
0.02032	0.00503	0.00499	0.00495
0.04022	0.00970	0.00962	0.00954
0.06668	0.01595	0.01581	0.01566
0.09176	0.02161	0.02142	0.02123

† Values at 25° C were extrapolated linearly from the experimental measurements at 30° and 35° C.

Carbon Tetrachloride/Methanol System

For the carbon tetrachloride/methanol system, three compositions at 26.5° C were studied from a low of 1.92% (mole) to a high of 4.9% (mole) carbon tetrachloride, as summarized in Table 4-9. Again the results show the trend of earlier experiments. As shown in Figure 4-10, the chemical potential derivatives from the centrifuge follow, but are consistently below the curve calculated from VLE data using the Wilson and

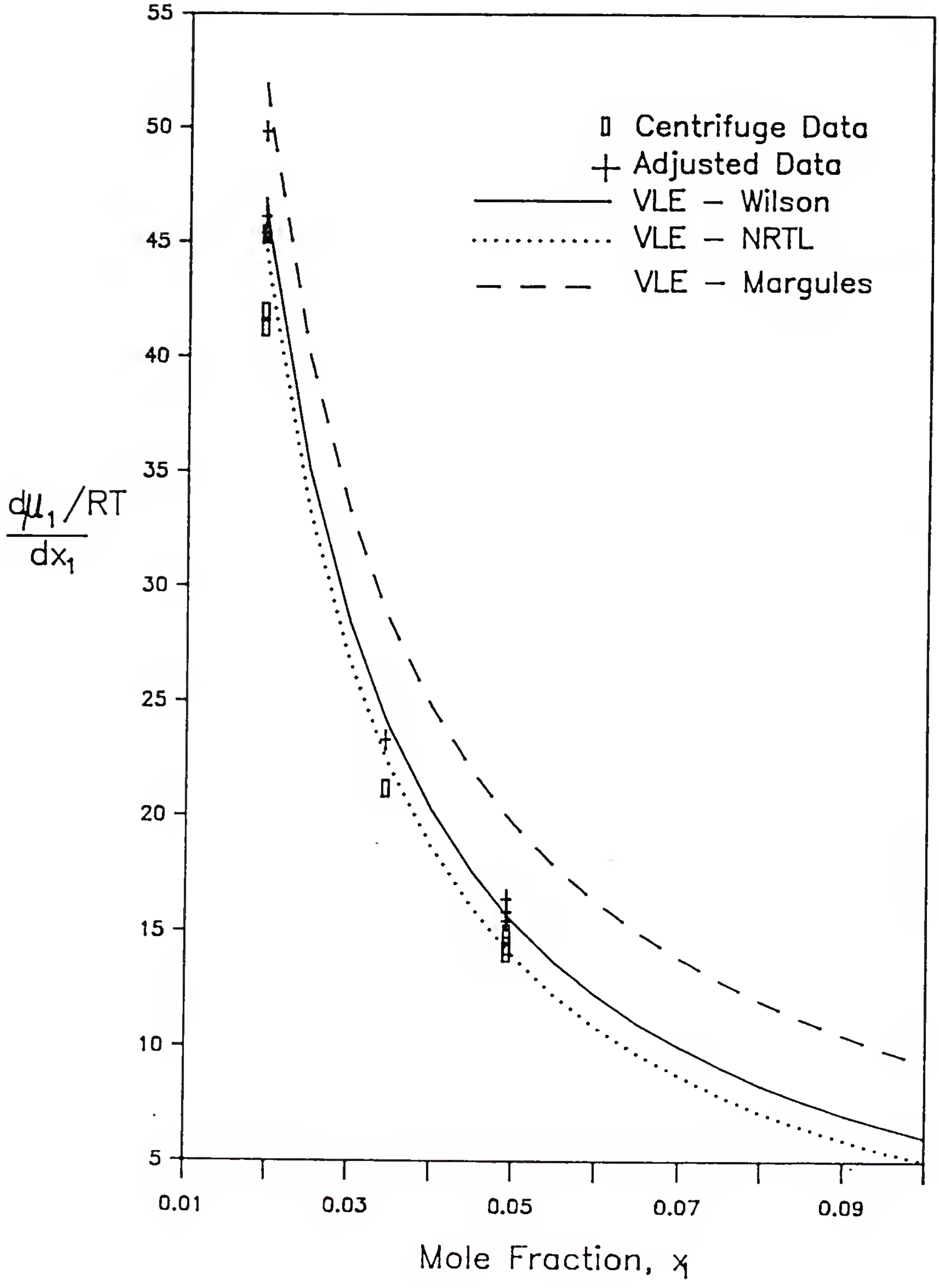

Figure 4-10 Chemical Potential Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Wolff and Hoeppel, 1968, at 20° C) Fitted to Various Models, for the System Carbon Tetrachloride(1) / Methanol(2).

NRTL equations with parameters regressed by Gmehling et al. (1977) and the data of Wolff and Hoeppel (1968).

Table 4-9
Summary of Carbon Tetrachloride(1)/Methanol(2)
Ultracentrifuge Experimental Results
and Comparison Values Calculated from Literature VLE Data

x_1^o	T °C	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Expt$^+$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Expt	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ Wlsn†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ Wlsn†	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$ NRTL†	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$ NRTL†
0.01923	26.5	-10.4±1.2	41.3	-5.080	46.92	-6.900	45.10
0.01923	26.5	-9.7±1.6	41.9				
0.01923	37.3	-6.2±5.8•	45.3				
0.03438	26.5	-7.6±2.7	21.2	-4.833	24.26	-6.468	22.62
0.04913	26.5	-5.4±1.1	14.9	-4.611	15.74	-6.082	14.27
0.04913	26.5	-5.9±0.8	14.4				
0.04913	37.3	-6.2±0.9	14.1				

+ Standard deviations from various fringes.
† Calculated from VLE data of Wolff and Hoeppel (1968) at 20° C.
• Appears inconsistant.

In this case the experimental values are closer to the VLE data than in other systems studied, but are still low by a factor of 1.1 which gives a reasonable fit to the VLE results (Figure 4-10). The activity coefficient derivatives calculated from the "corrected" chemical potential derivatives are shown in Figure 4-11.

One run was made at 37.3° C and 4.9% (mole) benzene. Statistically, its activity coefficient derivative was the same as the corresponding 26.5° C runs. This is consistant with the excess enthalpy which for this system is nearly zero (Abramov et al., 1973), when the solution has less than 20% carbon tetrachloride. Also, the VLE data of Wolff and Hoeppel (1968) show very little variation in the calculated activity coefficients or its derivative from 20° to 40° C. The run at 37.3° C and 1.9% (mole) benzene has a very high standard deviation and is obviously in error.

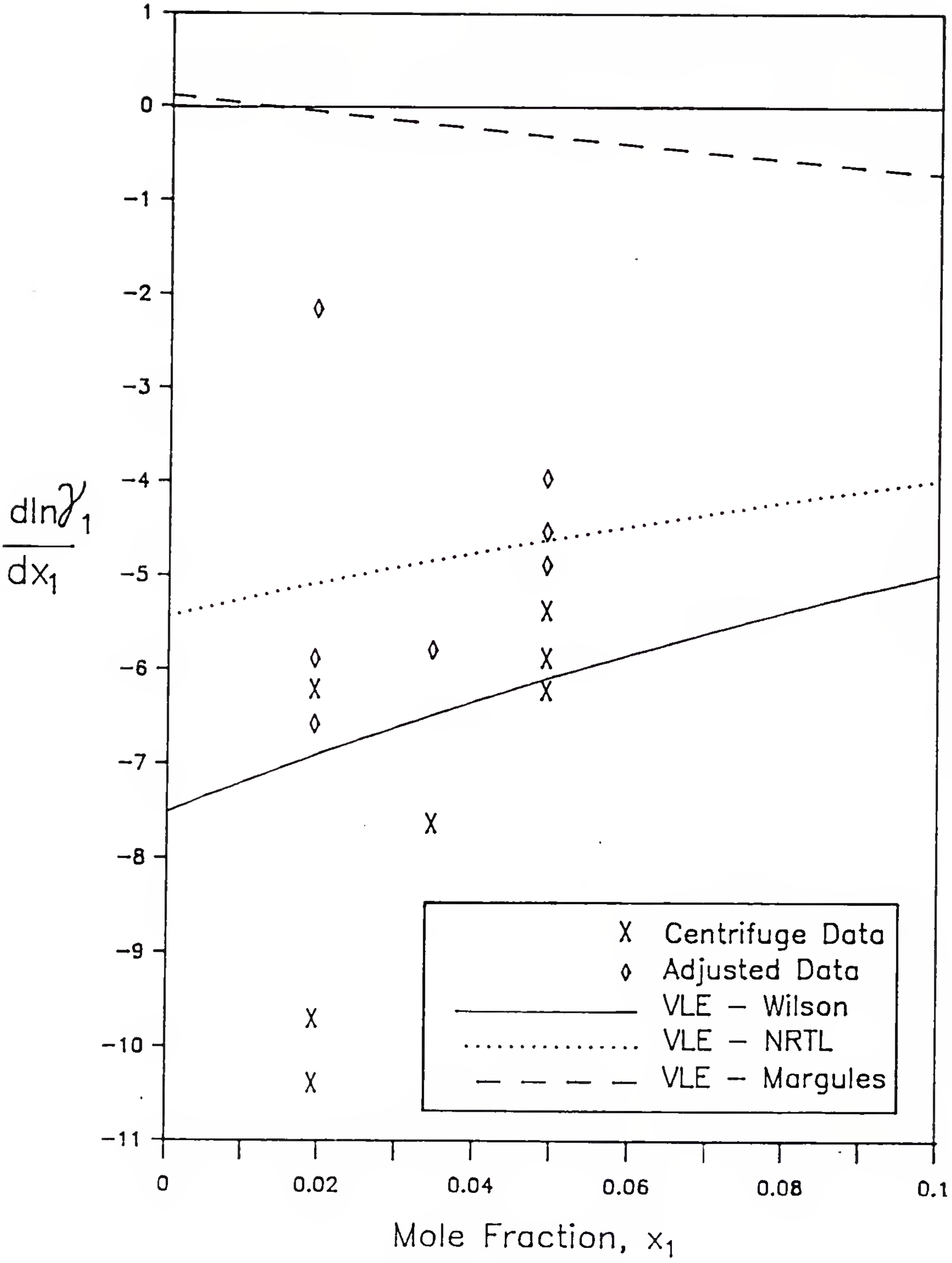

Figure 4-11 Activity Coefficient Derivatives From Ultracentrifuge Data (as Measured and Adjusted) and From VLE Data (Wolff and Hoeppel, 1968, at 20° C) Fitted to Various Models, for the System Carbon Tetrachloride(1) / Methanol(2).

There were no mixture refractive index data for this system available in the literature. The experimental data were measured at 30° and 35° C and extrapolated to other temperatures. This data is summarized in Table 4-10. Again, pure component refractive indexes were not used, so only the differential refractive index is given in Table 4-10.

Table 4-10
Differential Refractive Index (Δn) Experimental
Results for the System Carbon Tetrachloride(1)/Methanol(2)

x_1	Δn 25° C Extrap†	Δn 30° C Expt	Δn 35° C Expt
0.00000	0.00000	0.00000	0.00000
0.02389	0.00732	0.00720	0.00707
0.05500	0.01630	0.01606	0.01582

† Values at 25° C were extrapolated linearly from the experimental measurements at 30° and 35° C.

Summary of Experimental Results

Chemical potential derivatives measured in the ultracentrifuge for each of the five systems studied were lower than those calculated from VLE data. In each system a multiplicative factor would bring the results to within experimental error of the VLE curves. The factor was not the same for all systems, nor was it the same for all systems using acetone as a solvent. Experiments were made at different temperatures for all five systems. Generally the temperature effects on activity coefficient derivatives could not be distinguished for experimental uncertainties.

The results obtained are surprising and disappointing. The error analysis made for the method indicated more reliable results and a systematic deviation was unexpected. An analysis was made to determine the source of such systematic deviations. This included the effect of pressure and impurities.

Pressure Effects on the Results

Pressure in the cell during operation is a function of radius and speed. Thus, during a run at constant speed there is a considerable pressure gradient in the sample, and runs made at different speeds can have quite different average pressures. However, it was found that the experimental runs made at different speeds with the same sample were generally consistent (see Tables 4-1, 4-3, 4-5, 4-7 and 4-9). This indicates that pressure, which increases greatly with speed, had little effect on the results. However, to insure that pressure is not the cause of the experimental chemical potential derivatives being low, a more complete analysis was made.

Pressure is related to speed in a centrifugal field by the following expression

$$dP = \rho\, \omega^2\, r\, dr \tag*{(3-5}$$

Integrating equation (3-5) and using the values from Run 38-2 (see Appendix F), which are typical of the experiments run, the pressure varies from 1 atmosphere at the top to 42 atmospheres at the bottom. It is conceivable that such a pressure could affect the activity coefficient derivative calculation of equation 4-1 through the sedimentation parameter and the refractive index profile.

To illustrate the affect of pressure on the sedimentation parameter, the correlation of compressibility data of Winnick and Powers (1966) yields densities and partial molar volumes at the bottom of the cell under 42 atmospheres of pressure. The resulting sedimentation parameter is only 0.15% less than that at the surface, clearly a negligible difference. Cullinan and co-workers also concluded this for their studies (Sethy and Cullinan, 1972; Rau, 1975).

The pressure can also have an affect on the refractive index of fluids, causing the refractive index to vary differently in a spinning cell from a static composition variation. To determine the extent of the effect of pressure on the refractive index of fluids, measurements of pure fluids were made in the ultracentrifuge following the ideas of Richard (1980; Richard et al., 1979). The method entails loading a pure liquid sample in one side of the ultracentrifuge interference cell and air on the other side as a reference. When this cell is rotated in the ultracentrifuge the interference optics show a fringe pattern from the changing refractive index with increasing pressure through the cell. The pressure can be calculated at any depth in the cell using the integrated form of equation 3-5. The refractive index is known at the surface (1 atmosphere) and the refractive index increment to each fringe is known from equation 3-8. These yield the pure component refractive index as a function of pressure.

As an example, the results for acetone are given in Figure 4-12. While the data have some scatter caused by variations in microcomparator measurements, it is well described by a quadratic equation in pressure. The other pure components studied were adequately fit with a linear equation. The pressure coefficient of the refractive index, n, dn/dP, for carbon tetrachloride was found by Richard to be $5.5\text{x}10^{-5}$ atm^{-1}; here a value of $5.9\text{x}10^{-5}$ atm^{-1} was obtained. The agreement is probably within experimental error, indicating proper technique for this measurement.

Measurements were made on three of the solvents used here to determine the potential extent of pressure on refractive index profiles. Table 4-11 summarizes the measured data.

If a solvent and solute have the same linear change in refractive index with pressure (i.e., dn/dP constant), then the effect would not be observed since the change in the solution side of the double sector cell would be cancelled out by a change in the reference side of the cell. However, the different chemicals used do not have the same pressure variations, and acetone (the solvent in three systems) has a quadratic variation with pressure. The quadratic variation with pressure is particularly important because the reference (pure solvent) side of the cell is filled to a higher level than the sample (solution) side to insure that the interference pattern of the sample is fully covered by solvent. However, this means that the pressure throughout

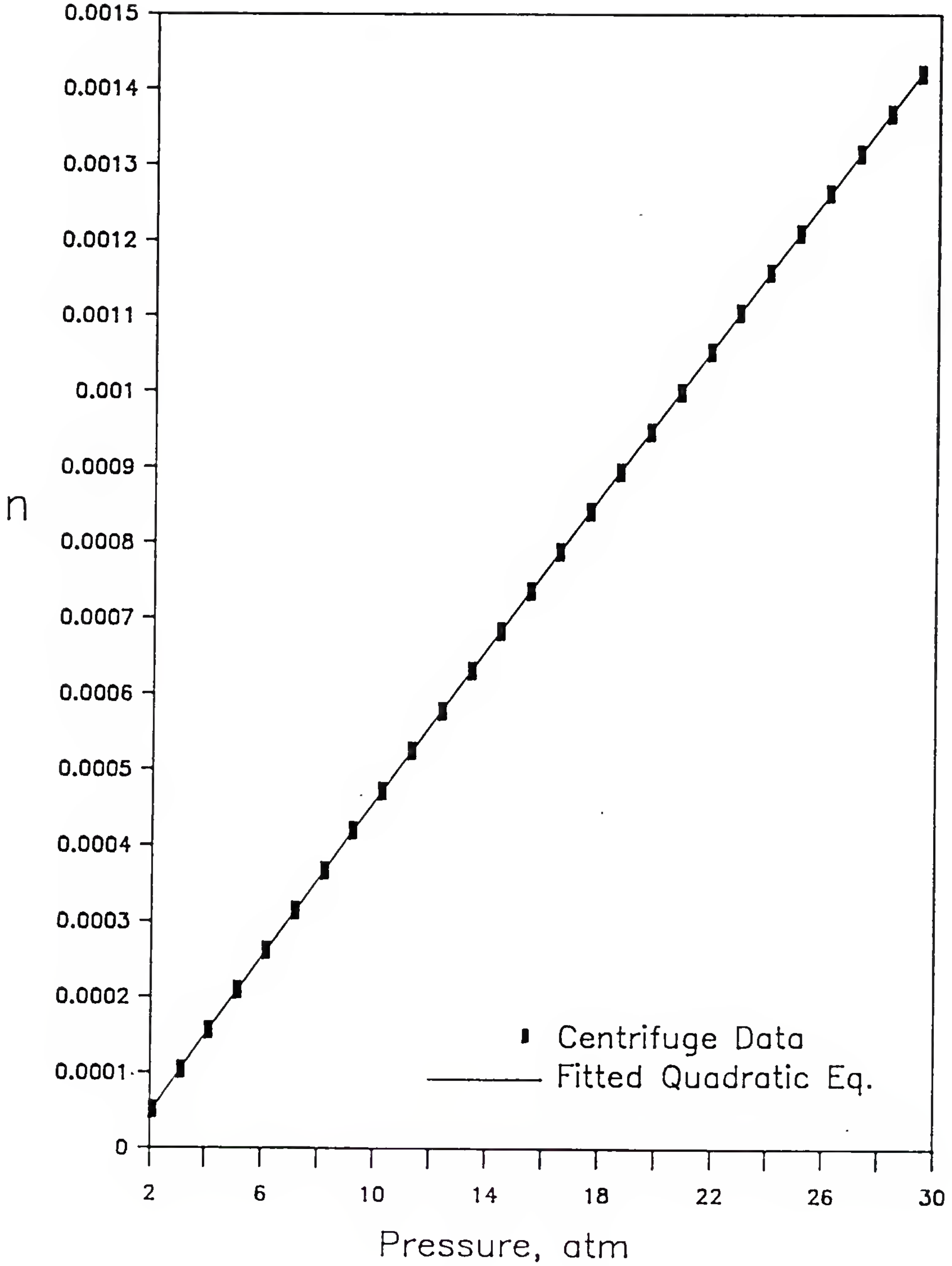

Figure 4-12 Pressure Effect on Refractive Index (n) as Measured in the Ultracentrifuge for Acetone at 25°.

the reference side is higher than the sample. Consequently, there can be no cancellation of effects, even when the dn/dP for the solute and solvent are the same.

Table 4-11
Experimental dn/dP Values

Compound	dn/dp x 10^5 atm^{-1}	Pressure Range atm
Acetone	5.0†	5 - 30
Chloroform	6.7	5 - 13
Chloroform	6.0	4 - 16
Carbon Disulfide	7.2	10 - 40
Carbon Tetrachloride	5.9	4 - 14

† Value given is at 20 atm, for acetone dn/dP is a function of pressure, $dn/dP[\text{atm}^{-1}] = 5.2\text{x}10^{-5} - P[\text{atm}]\text{x}10^{-7}$.

To quantitatively determine the magnitude of this effect, certain calculations were performed for carbon disulfide in acetone, and chloroform in acetone. Using the measured value of dn/dP, the change in refractive index due to pressure can be determined,

$$\Delta n_P \simeq \left(\frac{dn}{dP}\right)\Delta P \qquad (4\text{-}3$$

This can be calculated as an average over the entire cell or for each fringe, as is done in the computer program FRNGCNVP (see Appendix C). This calculation must be performed for both the pure solvent and the solution. In the solution a mole fraction average of the solvent and solute values of dn/dP is used. Using the relation of fringes to refractive index difference (equation 3-8) the change in the number of fringes due to pressure can be determined.

$$\Delta j_{P_i} = \Delta n_{P_i}\, d \,/\, \lambda \qquad (4\text{-}4$$

where i can be solvent or solute.

The net pressure effect on the fringes is found by subtracting the sample effect from the solvent effect.

$$\Delta j_P = \Delta j_P(\text{solvent}) - \Delta j_P(\text{sample}) \qquad \text{(4-5}$$

The result of this effect is summarized in Table 4-12 for the carbon disulfide in acetone and chloroform in acetone systems. The measured number of fringes for each run and the net effect of pressure on the number of fringes are given. In addition, the number of fringes necessary to match the ultracentrifuge activity coefficient derivatives with those derived from VLE data were computed and are listed. It is apparent that the effect of pressure on the refractive index is much smaller than the observed discrepancy.

Table 4-12
Fringe Adjustments Due to Pressure Effects
and Total Number of Fringes Required to Match
VLE Data In Two Typical Cases

x_1	Speed RPM	Fringes Actually Measured	Fringes with P Correction	Percent Change	Fringes to Match VLE	Percent Change
		Carbon Disulfide(1)/Acetone (2)				
0.03559	21739	4.85	4.68	3.5	3.83	21
0.03559	29502	8.94	8.2	8.3	7.14	20
0.03559	37000	14.02	12.12	13.6	11.27	20
		Chloroform(1)/Acetone(2)				
0.03713	25969	9.78	9.32	4.7	6.43	34
0.03713	29501	12.56	11.89	5.3	8.26	34
0.03713	37019	19.55	18.21	6.9	13.25	32

The Effect of Impurities on Ultracentrifugation

Certified spectrographic grade chemicals from Fisher have been used here. The acetone and acetonitrile were dried with Fisher molecular sieve 3 Å. Acetone was also tried without drying and no noticeable differences were found. Several factors can be considered. Impurities in the solute could not cause the discrepancy, their contribution would be too small. If an impurity only altered the solvent or solution refractive index, its effect would be taken care of by the measurement of refractive index in the differential refractometer, which used the same solvent samples as in the ultracentrifuge. Further, the effect would have been the same for all of the acetone systems, but it was not. Finally, any effect of a solvent impurity would be nearly a constant number of fringes at all concentrations of every solute, rather than a relative number as it was.

The only impurity known for the present chemicals was one small amount (0.75 %) of ethanol used as a stabilizer for the chloroform solute. However, since ethanol has a refractive index and density almost exactly the same as acetone (solvent), it would appear as more acetone and thus have no effect.

Summary

Determination of activity coefficient derivatives using laser interference optics in an analytical ultracentrifuge has been carried out on five systems. In all cases the experimental results were consistently lower than those calculated from vapor-liquid equilibrium data. In each system a single factor applied to the chemical potential derivative over the entire range of compositions matched the ultracentrifuge experimental quantities to the chemical potential derivatives calculated from VLE measurements. Investigation of pressure effects on the physical properties of the systems shows an insufficient corrective effect, while impurities in the chemicals also do not appear to be the cause.

Accepting a constant multiplicative factor for the ultracentrifuge data gives results which generally support the low concentration extrapolations of two equations (Wilson and NRTL) applied to VLE measurements. It was not possible to differentiate a best model for the VLE systems from the data measured here.

CHAPTER 5

DIRECT CORRELATION FUNCTION INTEGRAL DATABASE AND MODELING

Introduction

In an effort to develop new thermodynamic property models, free of common simplifying assumptions such as pairwise additivity of intermolecular forces and rigid molecules, the fluctuation solution approach has been taken by several authors (Kirkwood and Buff, 1951; O'Connell, 1971; 1981). Kirkwood and Buff (1951) formulated the density derivatives of the chemical potential and total system pressure in terms of integrals of the radial distribution function (g_{ij}). O'Connell (1971) used these formulations and the Ornstein and Zernike (1914) equations to give the fluctuation thermodynamic properties in terms of the direct correlation function integrals (DCFI or C_{ij}). These direct correlation functions appear relatively insensitive to the details of intermolecular interactions and may be modeled with simple functions. Additionally, because the thermodynamic properties are obtained by integration, the results can be much less sensitive to their parameterization. For example, Mathias and O'Connell (1979, 1981) found that this approach worked very well for gases dissolved in liquids.

The direct correlation function is given as

$$c_{ij} = h_{ij} - \Sigma_k \rho_k \int c_{ik} h_{jk} dr_k \qquad (5\text{-}1$$

where $h_{ij} \equiv g_{ij} - 1$, g_{ij} is the radial distribution function and ρ_k is the molar concentration of component k.

The density derivatives of the pressure and chemical potential or activity coefficient (shown here for component 1 of a binary system) are given as

$$\left(\frac{\partial P/RT}{\partial \rho_1}\right)_{T,\,\rho_2} = \frac{\overline{V}_1}{\kappa_T\, RT} = 1 - (\rho_1\, C_{11} + \rho_2\, C_{12}) \,/\, \rho \qquad (5\text{-}2$$

where $C_{ij} = \rho \int c_{ij}\, dr_{ij}$, is the direct correlation function integral.

$$\left(\frac{\partial P/RT}{\partial \rho}\right)_{T} = \frac{V}{\kappa_T\, RT} = 1 - (\rho_1^2\, C_{11} + 2\, \rho_1\, \rho_2\, C_{12} + \rho_2^2\, C_{22}) \,/\, \rho^2 \qquad (5\text{-}3$$

$$\left(\frac{\partial \mu_1/RT}{\partial \rho_1}\right)_{T,\,\rho_2} = \frac{1}{\rho_1} - \frac{C_{11}}{\rho} \qquad (5\text{-}4$$

$$\left(\frac{\partial \ln\gamma_1}{\partial \rho_1}\right)_{T,\,\rho_2} = (1 - C_{11}) \,/\, \rho \qquad (5\text{-}5$$

If the direct correlation function integrals can be modeled as functions of temperature and composition, integration of equations (5-2) and (5-4) can yield the pressure, solution density and the chemical potential, essential in phase equilibrium calculations. In particular, such a model may allow for accurate modeling of the activity coefficient of highly non-ideal systems.

The DCFIs modeled by Mathias and O'Connell (1979, 1981) work well for liquids containing supercritical components (dissolved gases) but apparently not as well for condensed phase systems (Campanella, 1984). Campanella made an attempt to model the DCFI for vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) systems in a fashion similar to that of Mathias (1978), using a hard sphere term and a perturbation term. He found in VLE systems that the hard sphere term did not show adequate compositional variation. Further, the data used to calculate DCFIs at low concentrations were not accurate enough to properly determine the compositional dependence in that region. His work was hindered by having to calculate activity coefficient derivatives indirectly by differentiating either tabulated phase equilibria data or data from a model, such as that of Wilson (1964). This has lead to uncertainty in the actual compositional behavior of DCFIs.

The objective of the present work has been to thoroughly explore the compositional behavior of the DCFI. The binary DCFIs can be written in terms of mole fraction and the measurable binary quantities of; isothermal compressibility, κ_T, partial molar volumes, $\overline{V}_1$ and $\overline{V}_2$, volume, V, and activity coefficient derivatives, $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P}$ and $\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,P}$

$$(1 - C_{11}) = \frac{\overline{V}_1^2}{V \kappa_T\, RT} + x_2 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} \qquad (5\text{-}6$$

$$(1 - C_{12}) = \frac{\overline{V}_1\, \overline{V}_2}{V \kappa_T\, RT} - x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} \qquad (5\text{-}7$$

$$(1 - C_{22}) = \frac{\overline{V}_2^2}{V \kappa_T\, RT} + x_1 \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,P} \qquad (5\text{-}8$$

Binary data on non-ideal systems have been collected, aided by the recent compilation of isothermal compressibilities by Huang (1986), and a database of DCFIs for a wide variety of systems has been created.

To compensate for the lack of directly measured activity coefficient derivative data, derivatives of the NRTL and Wilson models with parameters fit to VLE data will be used to cover the range of values for a given system. With these activity coefficient derivatives, a database of DCFIs can be developed. The sixteen non-ideal systems selected by Campanella (1984) plus twelve other non-ideal systems were chosen for study. For each of these systems, excess volume data, pure component compressibility data and vapor-liquid equilibrium data was obtained. For nineteen of the systems, mixture compressibility data was also available.

For modeling purposes, the DCFI can be conveniently divided into ideal and excess terms. The ideal DCFI is calculated by assuming an ideal mixing rule for the volume and isothermal compressibility. The activity coefficient derivative term is zero in the ideal case. By subtracting the ideal DCFI from the real DCFI, determined from experimental quantities, an excess quantity, resembling the activity coefficient derivative, remains. The ideal and excess DCFIs in a binary system are given as

$$(1 - C_{11})^{ID} = \frac{(V_1^o)^2}{(\, x_1\, V_1^o \kappa_{T1}^o + x_2\, V_2^o \kappa_{T2}^o)\, RT} \qquad (5\text{-}9$$

$$(1 - C_{12})^{ID} = \frac{V_1^o\; V_2^o}{(\, x_1\, V_1^o \kappa_{T1}^o + x_2\, V_2^o \kappa_{T2}^o)\, RT} \qquad (5\text{-}10$$

$$(1 - C_{22})^{ID} = \frac{(V_2^o)^2}{(\, x_1\, V_1^o\, \kappa_{T1}^o + x_2\, V_2^o\, \kappa_{T2}^o)\, RT} \qquad (5\text{-}11$$

$$(1 - C_{11})^E = (1 - C_{11}) - (1 - C_{11})^{ID} = f_{11}\, (v^E, \kappa_T^E) + x_2 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} \qquad (5\text{-}12$$

$$(1 - C_{12})^E = (1 - C_{12}) - (1 - C_{12})^{ID} = f_{21}\, (v^E, \kappa_T^E) - x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} \qquad (5\text{-}13$$

$$(1 - C_{22})^E = (1 - C_{22}) - (1 - C_{22})^{ID} = f_{22}\, (v^E, \kappa_T^E) + x_1 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \qquad (5\text{-}14$$

where the superscript ^{o} denotes pure component properties and f_{11}, f_{12} and f_{22} are functions of excess volume and excess compressibility. If this excess DCFI could be easily modeled it would lead to a better understanding of the compositional variation of the DCFI and aid future theoretical modeling efforts. Because the excess DCFI so closely resemble the activity coefficient derivatives, a modeling approach that uses a form similar to the derivatives of common activity coefficient models such as the Wilson (1964) or NRTL (Renon and Prausnitz, 1968) might prove beneficial. Indeed, Campanella (1984) pointed out that most of the activity coefficient models have a common form when written in terms of the composition derivative. For component 1 of a binary, three common models, Van Laar (Van Ness and Abbott, 1982), Wilson and NRTL, can be written as

Van Laar

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = \frac{\Phi x_2}{(x_1 \Theta + x_2 \Gamma)^2} + \frac{\Psi x_2^2}{(x_1 \Theta + x_2 \Gamma)^3} \qquad (5\text{-}15$$

where $\Phi = 2\, A_{12}\, A_{21}^2 \qquad \Theta = A_{12} \qquad \Gamma = A_{21} \qquad \Psi = 2\, A_{21}^2\, A_{12}\, (A_{21} - A_{12})$

A_{12} and A_{21} are Van Laar model binary parameters.

Wilson

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = \sum_{i=1}^{2} \frac{\Phi_i}{x_1\Theta_i + x_2\Gamma_i} + \sum_{i=1}^{2} \frac{\Psi_i x_2}{(x_1\Theta_i + x_2\Gamma_i)^2} \qquad \text{(5-16}$$

where $\Phi_1 = -1$ $\Theta_1 = 1$ $\Gamma_1 = \Lambda_{12}$ $\Psi_1 = \Lambda_{12}(\Lambda_{12} - 1)$

$\Phi_2 = \Lambda_{21}$ $\Theta_2 = \Lambda_{21}$ $\Gamma_2 = 1$ $\Psi_2 = \Lambda_{21}(\Lambda_{21} - 1)$

Λ_{12} and Λ_{21} are Wilson model binary parameters.

NRTL

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = \sum_{i=1}^{2} \frac{\Phi_i x_2}{(x_1\Theta_i + x_2\Gamma_i)^2} + \sum_{i=1}^{2} \frac{\Psi_i x_2^2}{(x_1\Theta_i + x_2\Gamma_i)^3} \qquad \text{(5-16}$$

where $\Phi_1 = 2\,\tau_{21}\,G_{21}^2$ $\Theta_1 = 1$ $\Gamma_1 = G_{21}$ $\Psi_1 = 2\,\tau_{21}\,G_{21}^2\,(G_{21} - 1)$

$\Phi_2 = 2\,\tau_{12}\,G_{12}$ $\Theta_2 = G_{12}$ $\Gamma_2 = 1$ $\Psi_2 = 2\,\tau_{12}\,G_{12}\,(G_{12} - 1)$

τ_{12}, τ_{21}, G_{12} and G_{21} are NRTL model binary parameters.

The common term here, $\dfrac{\Phi x_2^n}{(x_1\Theta + x_2\Gamma)^m}$, may work well as a model for the excess DCFI.

The activity coefficient derivative of component 1 in a binary system can be written directly in terms of the three binary DCFIs and the reduced bulk modulus as

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = x_2\,[(1 - C_{11})(1 - C_{22}) - (1 - C_{12})^2]\,\rho\,\kappa_T\,RT \qquad \text{(5-18}$$

Examination of this grouping of DCFIs calculated from the database may suggest a new empirical relationship for the activity coefficient derivative.

DCFI Database

The database of DCFIs includes only significantly non-ideal systems. These types of systems will have the largest and most complicated excess terms. Campanella (1984) studied many systems, both ideal and non-ideal. He found the ideal systems to be simple and easily modeled with the ideal DCFI. However, his study of non-ideal systems was limited by the availability of good data. For the present study the sixteen non-ideal systems selected by Campanella (1984) have been reexamined with better data. Twelve additional systems for which complete data could be located are also included.

The criteria for inclusion of a compound in the database includes the availability of pure component and excess volumes, pure component and mixture isothermal compressibilities and vapor-liquid equilibrium (VLE) data for the binary pair over the entire range of composition at a single temperature. If mixture excess volume was not available at the chosen temperature, it was interpolated or extrapolated over small temperature differences. A system was included only when all of these data could be obtained at a common temperature.

Pure component volumes were taken from the data compilation of DIPPR (American Institute of Chemical Engineers', Design Institute for Physical Property Research) (Daubert and Danner, 1985). Excess volume parameters were primarily taken from the compilation by Handa and Benson (1979). If isothermal compressibility data at low pressure were available for the mixture, it was used directly. Otherwise pure component and mixture liquid pressure, volume and temperature (PVT) data were used to regress parameters to the liquid equation of state developed by Huang (1986). Huang's equation of state can then be used to calculate isothermal compressibility. Sources of PVT data for pure components and mixtures were taken from the review by Tekac et al. (1985). In all but two cases, isothermal VLE data model parameters were collected from the data compilation of Gmehling et al. (1977). When more than one set of VLE data was available from Gmehling et al. (1977), their recommendation (if given) was used, otherwise the data set with the lowest sum of errors in their regression was used. Tables 5-1 and 5-2 give a summary of parameter and data sources for excess volumes and VLE.

Table 5-1
Excess Volume References for Binary Systems in Database

	Component	Formula	Component	Formula	Temperature °C	Excess Volume Reference	v^E Meth.†
1	Carbon Tetrachloride	CCl_4	Methanol	CH_4O	20	Ocon, et al., (1969)	1
2	Carbon Tetrachloride	CCl_4	Acetonitrile	C_2H_3N	45	Kalliorinne (1969)	2
3	Carbon Tetrachloride	CCl_4	Ethanol	C_2H_6O	20	Varma, et al. (1976)	2
4	Carbon Tetrachloride	CCl_4	Acetone	C_3H_6O	45	Nigam et al. (1972)	3
5	Carbon Tetrachloride	CCl_4	THF	C_4H_8O	25	Guillen and Losa (1978)	2
6	Carbon Tetrachloride	CCl_4	Aniline	C_6H_7N	25	Katz et al. (1973)	1
7	Methanol	CH_4O	Water	H_2O	40	Mikhail and Kimel (1961)	5
8	Chloroform	$CHCl_3$	Methanol	CH_4O	35	Winnick and Kong (1974)	6
9	Chloroform	$CHCl_3$	Ethyl Ether	C_2H_6O	25	Nigam et al. (1972)	1
10	Chloroform	$CHCl_3$	Acetone	C_3H_6O	25	Nigam et al. (1972)	1
11	Carbon Disulfide	CS_2	Acetone	C_3H_6O	25	Nigam et al. (1972)	1
12	Acetonitrile	C_2H_3N	Benzene	C_6H_6	45	Palmer and Smith (1972)	1
13	1,2-dichloroethane	$C_2H_4Cl_2$	Benzene	C_6H_6	20	Kiyohara and Arakawa (1970)	1
14	Ethanol	C_2H_6O	Cyclohexane	C_6H_{12}	10	Marsh and Burfitt (1975)	4
15	Ethanol	C_2H_6O	Benzene	C_6H_6	25	Marsh and Burfitt (1975)	4
16	Ethanol	C_2H_6O	Heptane	C_7H_{16}	30	Treszczanowicz and Benson (1977)	4,6 [25°C]
17	Ethanol	C_2H_6O	Water	H_2O	40	Perry and Chilton (1973)	5
18	Acetone	C_3H_6O	Benzene	C_6H_6	25	Nigam et al. (1972)	1
19	Acetone	C_3H_6O	Water	H_2O	25	Boje and Hvidt (1971)	1
20	Propanol	C_3H_8O	Water	H_2O	30	Mikhail and Kimel (1963)	5
21	1,4-Dioxane	$C_4H_8O_2$	Benzene	C_6H_6	25	Andrews and Morcom (1971)	1
22	Cyclopentane	C_5H_{10}	Cycloctane	C_8H_{16}	25	Ewing, et al. (1970)	5
23	Cyclopentane	C_5H_{10}	OMCTS	$C_8H_{20}O_4Si_4$	25	Marsh (1970)	1‡
24	Pyridine	C_5H_5N	Benzene	C_6H_6	25	Garrett, et al. (1973)	1
25	Chlorobenzene	C_6H_5Cl	Aniline	C_6H_7N	25	Deshpande and Bhatgadde (1968)	5
26	Nitobenzene	$C_6H_5NO_2$	Aniline	C_6H_7N	60	Miller, et al. (1975)	6 [25°C]
27	Benzene	C_6H_6	Aniline	C_6H_7N	25	Deshpande and Bhatgadde (1968)	5
28	Aniline	C_6H_7N	Toluene	C_7H_8	20	Katz, et al. (1971)	3

†Excess Volume Methods

1. Use Handa and Benson (1979) (‡ or original author) parameters directly or change variables from x_1 to x_2.
2. Interpolate data by recalculating data at other temperatures from Handa and Benson parameters and refitting with simple least squares.
3. Extrapolate data by recalculating data at other temperatures from Handa and Benson parameters and refitting with simple least squares.
4. Generate data from a different Handa and Benson equation and refit with simple least squates.
5. Fit original data by simple least squares.
6. Use only Handa and Benson parameters available at a different temperature, indicated on the table in brackets.

Table 5-2
Vapor-Liquid Equilibria References for Binary Systems in the DCFI Database

Component	Formula	Component	Formula	Temperature °C	Vapor-Liquid Equilibria Reference
1 Carbon Tetrachloride	CCl_4	Methanol	CH_4O	20	Wolff and Hoppel (1968)
2 Carbon Tetrachloride	CCl_4	Acetonitrile	C_2H_3N	45	Brown and Smith (1954)
3 Carbon Tetrachloride	CCl_4	Ethanol	C_2H_6O	20	Niini (1940)
4 Carbon Tetrachloride	CCl_4	Acetone	C_3H_6O	45	Brown and Smith (1957)
5 Carbon Tetrachloride	CCl_4	THF	C_4H_8O	25	Becker, et al. (1974)
6 Carbon Tetrachloride	CCl_4	Aniline	C_6H_7N	25	Deshpande and Pandya (1967)
7 Methanol	CH_4O	Water	H_2O	40	Ratcliff and Chao (1969)
8 Chloroform	$CHCl_3$	Methanol	CH_4O	35	Kireev and Sitnikov (1941)
9 Chloroform	$CHCl_3$	Ethyl Ether	C_2H_6O	25	Becker et al. (1974)
10 Chloroform	$CHCl_3$	Acetone	C_3H_6O	25	Rabinovich and Nikolaev (1960)
11 Carbon Disulfide	CS_2	Acetone	C_3H_6O	25	Litvinov (1952)
12 Acetonitrile	C_2H_3N	Benzene	C_6H_6	45	Brown and Smith (1955)
13 1,2-dichloroethane	$C_2H_4Cl_2$	Benzene	C_6H_6	20	Sieg et al. (1951)
14 Ethanol	C_2H_6O	Cyclohexane	C_6H_{12}	10	Nagai and Isii (1935)
15 Ethanol	C_2H_6O	Benzene	C_6H_6	25	Niini (1940)
16 Ethanol	C_2H_6O	Heptane	C_7H_{16}	30	Ponc and Ratcliff (1976)
17 Ethanol	C_2H_6O	Water	H_2O	40	Mertl (1972)
18 Acetone	C_3H_6O	Benzene	C_6H_6	25	Tasci et al. (1978)
19 Acetone	C_3H_6O	Water	H_2O	25	Beare et al. (1930)
20 Propanol	C_3H_6O	Water	H_2O	30	Ucovenko and Mazanko (1972)
21 1,4-Dioxane	$C_4H_8O_2$	Benzene	C_6H_6	25	Deshpande and Oswal (1972)
22 Cyclopentane	C_5H_{10}	Cycloctane	C_8H_{16}	25	Ewing et al. (1970)†
23 Cyclopentane	C_5H_{10}	OMCTS	$C_8H_{20}O_4Si_4$	25	Marsh (1970)†
24 Pyridine	C_5H_5N	Benzene	C_6H_6	25	Garrett et al. (1973)
25 Chlorobenzene	C_6H_5Cl	Aniline	C_6H_7N	25	Deshpande and Pandya (1967)
26 Nitobenzene	$C_6H_5NO_2$	Aniline	C_6H_7N	60	Holtzlander and Riggle (1955)‡
27 Benzene	C_6H_6	Aniline	C_6H_7N	25	Deshpande and Pandya (1967)
28 Aniline	C_6H_7N	Toluene	C_7H_8	20	Billes and Varsanyi (1963)

Binary Parameters for the above systems were taken from the compilation of Gmehling et al. (1977) unless otherwise stated.
†Original data regressed in this study by Generalized Least Squares.
‡Data for this system is isobaric at 5mm Hg pressure over a temperature range of 58° to 69° C.

Isothermal Compressibility Data

When mixture isothermal compressibility data was not available, pure component PVT data was fit to the liquid equation of state, given by Huang (1986) using the regression method of generalized least squares (see Appendix G for an explanation of the method and a listing of the FORTRAN computer program). The equation of state is given as

$$P = P_o + \rho^* RT \{(\tilde{\rho} - \tilde{\rho}_o) - C^* [(9.8642 - \frac{10.191}{\tilde{T}} - \frac{1.5356}{\tilde{T}^2})(\tilde{\rho} - \tilde{\rho}_o) - (14.2325 - \frac{15.432}{\tilde{T}} - \frac{3.0147}{\tilde{T}^2})(\tilde{\rho}^2 - \tilde{\rho}_o^2) + (9.18067 - \frac{10.966}{\tilde{T}} - \frac{2.90433}{\tilde{T}^2})(\tilde{\rho}^3 - \tilde{\rho}_o^3) - (2.06515 - \frac{3.18425}{\tilde{T}} - \frac{1.00425}{\tilde{T}^2})(\tilde{\rho}^4 - \tilde{\rho}_o^4)]\} \tag*{(5-19}$$

where P_o is the pressure at ρ_o and T, $\tilde{T} = T / T^*$, $\tilde{\rho} = \rho / \rho^*$ and C^*, T^* and ρ^* are characteristic parameters.

Using the definition of isothermal compressibility, κ_T ,

$$\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \quad \text{or } \kappa_T^{-1} = \rho \left(\frac{\partial P}{\partial \rho}\right)_T \tag*{(5-20}$$

equation (5-19) can be used to calculate κ_T.

$$\kappa_T^{-1} = \rho RT \{1 - C^* [(9.8642 - \frac{10.191}{\tilde{T}} - \frac{1.5356}{\tilde{T}^2}) - (28.4655 - \frac{30.864}{\tilde{T}} - \frac{6.0294}{\tilde{T}^2})\tilde{\rho} + (27.542 - \frac{32.898}{\tilde{T}} - \frac{8.7130}{\tilde{T}^2})\tilde{\rho}^2 - (8.2606 - \frac{12.737}{\tilde{T}} - \frac{4.0170}{\tilde{T}^2})\tilde{\rho}^3]\} \tag*{(5-21}$$

Huang (1986) gives mixing rules, which for a binary can be written as,

$$V_M^* = x_1^2 V_1^* + x_2^2 V_2^* + x_1 x_2 (V_1 + V_2)(1 - k_{12}) \tag*{(5-22}$$

$$C_M^* = x_1 C_1^* + x_2 C_2^* \tag*{(5-23}$$

$$T_M^* = x_1 T_1^* + x_2 T_2^* \tag*{(5-24}$$

where k_{12} is a binary interaction parameter. When binary PVT data were available, they were used to regress the binary parameter, k_{12}. It was found that the results were much better if pure component parameters were fit to all of the pure data available and only mixture data was used to obtain k_{12}. If binary data were not available, k_{12} was assumed to be zero. According to Huang (1986) this gives a good approximation of the mixture compressibility.

Pure component and binary parameters regressed by generalized least squares to the equation of state (5-19) of Huang (1986) are summarized in Tables 5-3 and 5-4. The parameters listed are slightly different than those of Huang, because data was combined from more than one source to give a single set of parameters for each compound. Parameters for 1,4-dioxane, propanol and cyclooctane were not reported by Huang (1986) nor were most of the binary parameters given here.

Much of the binary liquid PVT data used here needed to be manipulated in some manner to get it into a suitable form for regression. In some cases the mixture data had to be adjusted so as to be more consistent with the pure component parameters. In all cases the pure component parameters were regressed to pure component data only. In some cases if the pure component data from a source giving mixture data appeared consistent, they were included in the pure component database. If not consistent, special treatment was done. The following describes the regression of binary parameters included in Table 5-4.

The only mixture data available for the carbon tetrachloride/acetonitrile system are from Hanks et al. (1978) over a range of pressure from 28 to 220 bars and at temperatures of 0°, 45° and 90° C. The pure data for carbon tetrachloride (Hanks et al, 1978) and acetonitrile (Gupta and Hanks, 1977), taken in this same study, were not consistent with the pure component parameters. Further, if their pure component data were regressed alone, they gave quite different results than the other sources of data used for carbon tetrachloride and acetonitrile (see Table 5-3). To compensate for this disparity, the volume was calculated at 0° and 45° C and at the pressures used by Hanks et al. (1978), using equation (5-21) along with the pure component parameters from Table 5-3 and pure component reference volumes at one atmosphere from

Table 5-3
Liquid Equation of State (5-19) Pure Component Parameters

Empirical Formula	Compound Name	C^*	V^* cc/gmol	T^* K	Error† cc/gmol	Pressure Range bars	Temperature Range K	Reference
CCl_4	Carbon Tetrachloride	-42.390	95.502	499.72	0.044	0, 2622	273, 373	Gibson and Loeffler (1941) Mopsik (1969) Benson and Winnick (1976) Hanks et al. (1978)‡
CS_2	Carbon Disulfide	-28.632	59.711	429.29	0.018	1, 2028	223, 298	Mopsik (1969) Bridgman (1913)‡
$CHCl_3$	Chloroform	-50.565	76.215	443.01	0.042	.1, 4000	273, 363	Schroeder et al. (1978) Kumagai and Takahaski (1982) Burkat and Richard (1975)
CH_4O	Methanol	-13.856	40.337	499.05	0.058	1, 2750	283, 473	Buck (1978) Kubota et al. (1979) Machado and Street (1983) Easteal and Woolf (1985) Seitz and Lechner (1916)‡
C_2H_3N	Acetonitrile	-12.750	55.414	486.04	0.104	1, 4500	283, 333	Schroeder et al. (1977) Srinivasan and Kay (1977) Gupta and Hanks (1977)‡
$C_2H_4Cl_2$	1,2-Dichloro ethane	-28.908	82.533	519.1	0.016	.3, 1013	298, 398	Kumagai and Takahaski (1985)
C_2H_6O	Ethanol	-23.744	57.834	508.26	0.077	1, 3104	298, 348	Ozawa et al. (1980) Tanaka et al. (1977) Bridgman (1913)‡ Gupta and Hanks (1977)‡
C_2H_6O	Ethyl Ether	-45.087	96.710	409.64	0.123	1, 12160	293, 353	Bridgman (1913)
C_3H_6O	Acetone	-34.849	72.315	555.00	0.07	10, 4118	298, 398	Ratzsch and Findeisen (1980) Atoyan and Mamedov (1976)‡ Gupta and Hanks (1977)‡
C_3H_8O	n-Propanol	-119.385	69.106	566.04	0.003	1, 61	293, 298	Sahli et al. (1976)
C_4H_8O	THF	-162.470	65.412	295.74	0.348	1, 5170	303, 323	Schornack and Eckert (1970)
$C_4H_8O_2$	1,4-Dioxane	-7.878	109.446	587††	0.012	0, 1000	298	Pearce and Strauss (1968)
C_5H_5N	Pyridine	-34.734	84.104	574.77	0.053	1, 4000	303, 423	Fury et al. (1979)
C_5H_{10}	Cyclopentane	-26.668	95.65	530.43	0.008	1, 1961	298, 353	Kuss and Taslimi (1970)
C_6H_5Cl	Chlorobenzene	-39.908	106.070	552.56	0.006	0, 1000	298, 358	Gibson and Loeffler (1939b) Schornack and Eckert (1970)‡
$C_6H_5NO_2$	Nitobenzene	-49.285	108.920	575	0.011	0, 1000	293, 358	Gibson and Loeffler (1939b) Takagi and Teranishi (1982a;b)

Table 5-3 Continued

Empirical Formula	Compound Name	C^*	V^* cc/gmol	T^* K	Error† cc/gmol	Pressure Range bars	Temperature Range K	Reference
C_6H_6	Benzene	-55.725	85.524	473.37	0.061	0, 4000	288, 433	Gibson and Loeffler (1941) Parkhurst and Jonas (1975a) Parkhurst and Jonas (1975b) Dymond et al. (1982) Kashiwagi et al. (1979) Takagi (1978) Matsuo and Van Hook (1984) Glanville and Sage (1949)‡ Takagi and Teranishi (1982a)‡ Dymond et al. (1981)‡ Gupta and Hanks (1977)‡
C_6H_7N	Aniline	-47.906	96.924	577.48	0.004	0, 1000	298, 358	Gibson and Loeffler (1939b)
C_6H_{12}	Cyclohexane	-54.854	104.96	492.36	0.038	1, 1100	286, 353	Burkat and Richard (1975) Wisotzki and Wurflinger (1982) Kashiwagi et al. (1979) Isdale et al. (1979) Kuss and Taslimi (1970) Matsuo and Van Hook (1984) Reamer and Sage (1957)‡ Jonas et al. (1980)‡
C_7H_8	Toluene	-67.501	102.72	470.34	0.046	1, 2028	223, 313	Mopsik (1969) Takagi (1978)
C_7H_{16}	n-Heptane	-67.389	139.354	453.10	0.14	0, 5066	273, 393	Eduljee et al. (1951) Boelhouwer (1960) Kuss and Taslimi (1970) Ozawa et al. (1980) Doolittle (1964)
C_8H_{16}	Cycloctane	-59.964	137.740	595.48	0.025	51, 401	313, 393	Gouel (1978)
$C_8H_{20}O_4Si_4$	OMCTS	-137.960	297.020	489.18	0.104	1, 1662	313, 373	Benson and Winnick (1976)
H_2O	Water	-17.162	17.162	319.27	0.008	0, 2077	273, 373	Chen et al. (1977) Kubota et al. (1979) Gibson and Loeffler (1941) Lamb and Hunt (1977)‡ Tanaka et al. (1977)‡

Notes:

† Average absolute error in recalculated volumes.

†† Only isothermal data was available, therefore T^* was set equal to the compound critical temperature.

‡ This reference was considered, but not used.

Table 5-4
Liquid Equation of State (5-19) Binary Parameters (k_{12})

Empirical Formula	System	k_{12}	Error* cc/gmol	Pressure Range bars	Temperature Range K	Reference
CCl_4 C_2H_3N	†Carbon Tetrachloride Acetonitrile	-0.0364	0.03	28, 220	273, 318	Hanks et al. (1978)
CCl_4 C_3H_6O	†Carbon Tetrachloride Acetone	-0.028	0.058	28, 220	273, 318	Hanks et al. (1978)
CH_4O H_2O	Methanol Water	0.0231	0.057	1, 2058	283, 348	Kubota et al. (1979)
$CHCl_3$ C_3H_6O	†Chloroform Acetone	0.0034	0.004	1013	298	Newitt and Weale (1951)
C_2H_3N C_6H_6	†Acetonitrile Benzene	0.017	0.039	28, 220	318	Gupta and Hanks (1977)
C_2H_6O C_6H_6	†Ethanol Benzene	0.0139	0.027	28, 220	318	Gupta and Hanks (1977)
C_2H_6O C_7H_{16}	Ethanol n-Heptane	-0.0059	0.07	1, 1962	298, 348	Ozawa et al. (1980)
C_2H_6O H_2O	Ethanol Water	0.0038	0.07	1, 3140	298, 323	Tanaka et al. (1977)
C_3H_6O C_6H_6	†Acetone Benzene	-0.0392	0.03	28, 220	318	Hanks et al. (1978)
C_3H_6O H_2O	†Acetone Water	-0.0064	0.058	1014	298	Newitt and Weale (1951)
C_3H_8O H_2O	†n-Propanol Water	-0.0152	0.07	1014	298	Nakagawa et al. (1983) Newitt and Weale (1951)‡

Notes:

* Average absolute error in recalculated volumes.
† Volumes were adjusted to meet the pure component volumes calculated by equation 5-19.
‡ This reference was considered, but not used.

DIPPR (Daubert and Danner, 1985). The mixture volumes were then adjusted as a mole fraction average of the two pure component adjustments. The pure component adjustments are the differences between the calculated volumes and the volumes reported by the original authors. Using reference volumes at one atmosphere calculated from the DIPPR pure component properties and excess volume data, the binary parameter, k_{12}, was regressed. The reference excess volume for this system was extrapolated to 0° C and interpolated to 45° C from data in the temperature range of 15° to 50° C (parameters from Handa and Benson, 1979; data from Nigam et al., 1972). When the adjusted mixture volumes were recalculated using this binary parameter the average absolute difference was 0.03 cc/gmole.

For the system carbon tetrachloride/acetone the only data were again from Hanks et al. (1978) over the range of pressure from 28 to 220 bars and at temperatures of 0°, 45° and 90° C. The pure component data of Gupta and Hanks (1977) and Hanks et al. (1978) were inconsistent as above. The same adjustments were made to this set of data, based on pure component calculations of carbon tetrachloride and acetone volumes, as in the previous system. Again, DIPPR (Daubert and Danner, 1985) data were used as the pure component reference at one atmosphere. Excess volume data at one atmosphere were extrapolated to 0° and 45° C from Nigam et al. (1972) (data) and Handa and Benson (1979) (parameters). The result of using the reported binary parameter is an average absolute error in the recalculation of adjusted volumes of 0.058 cc/gmole.

Pure component water and methanol data of Kubota et al. (1979) were among the data used to regress both pure component parameters. Therefore, the mixture data of Kubota et al. (1979), over the pressure range of 1 to 2058 bars and temperatures of 10° to 75° C, were simply regressed for a binary parameter. The result was an error in recalculated volumes of 0.057 cc/gmole.

Mixture isothermal compressibility data for the chloroform/diethyl ether system were reported directly by Dolezalek and Speidel (1920) at a temperature of 24.6° C and pressures from 25 to 588 bars. All calculations for the database were needed at one bar pressure. To adjust for pressure, the isothermal compressibility at each composition given was fit to a cubic equation in pressure, and extrapolated to one bar pressure.

Chloroform/acetone mixture compressions (k) were given by Newitt and Weale (1951) at 25° C and 1000 atmospheres pressure. Compressions are related to volume by

$$V = V_o - V_o k \tag{5-25}$$

where V_o is the volume at low pressure. Using parameters from Table 5-3 along with reference pure component volumes at one atmosphere from DIPPR and excess volumes from Nigam et al. (1972) (data) and Handa and Benson (1979) (parameters), the volumes at 1000 atmospheres were calculated with equation (5-19). The pure component volumes calculated from compressions did not correspond with those calculated from equation (5-19). The mixture volumes were then adjusted as a mole fraction average of the pure component adjustments and the binary parameter was regressed. The result was a recalculation of the mixture volumes with only a 0.004 cc/gmole average absolute error.

For the acetonitrile/benzene system, the only mixture data available were that of Gupta and Hanks (1977) over a pressure range of 28 to 220 bars and at temperatures of 0°, 45° and 90° C. As with all of the data from these authors, the mixture volumes were adjusted. Only the data at 45° C were used, as 90° C is too far from the normal conditions of interest, and pure component measurements were not made at 0° C. Using as a reference pure component volumes of DIPPR and excess volumes of Palmer and Smith (1972) (data) and Handa and Benson (1979) (parameters), a binary parameter was regressed from the adjusted volumes. Recalculating the volumes with the binary parameter resulted in an average absolute error of 0.039 cc/gmole.

Ethanol and benzene mixture data were also from Gupta and Hanks (1977), over a pressure range of 28 to 220 bars and at temperatures of 0°, 45° and 90° C, and showed the same problems as other data from these authors. The mixture data were adjusted and regressed, using volumes at one atmosphere from pure data of DIPPR and excess volumes from Treszczanowicz and Benson (1977) (data) and Handa and Benson (1979) (parameters) as reference data. Recalculating the volumes with the regressed binary parameter resulted in an average absolute error of 0.027 cc/gmole.

For ethanol/heptane the data of Ozawa et al. (1980) were used in the regression of both pure components. Therefore, the mixture data (over a pressure range of 1 to 1962 bars and temperatures from 25° to 75° C) were simply regressed, resulting in an average absolute error in recalculated volumes of 0.07 cc/gmole.

The data of Tanaka et al. (1977) were used in the regression of pure component parameters for ethanol, but not for water. However, fitting the ethanol/water mixture data over a pressure range of 1 to 3140 bars and at temperatures of 25° and 50° C, a single binary parameter gave a reasonable fit. The average absolute error in calculated volumes was 0.02 cc/gmole for pure water and 0.07 cc/gmole for the mixture volumes.

Mixture data for benzene and acetone were measured only by Hanks et al. (1978). Again the volumes were adjusted at 45° C using the pure component reference volumes at one atmosphere of DIPPR and excess volumes of Nigam et al. (1972) (data) and Handa and Benson (1979) (parameters). Using the regressed binary parameter, the resulting error in calculating mixture volumes was 0.03 cc/gmole.

Newitt and Weale (1951) also reported compression (k) data on the system acetone/water at 25° C and 1000 atmospheres. This data was handled in the manner described above for the acetone/chloroform data from these authors. Again, the volumes were adjusted to meet pure component volumes and a binary parameter was regressed. The resulting error in calculated mixture volumes was 0.058 cc/gmole.

Newitt and Weale (1951) and Nakagawa et al. (1983) both report compressions for the system n-propanol/water at 25° C and 1000 atmospheres. Both sets of data were handled in the same fashion as above. Both were adjusted to meet pure component volumes using low pressure volumes from DIPPR and excess volume data of Mikhail and Kimel (1963) as references. The Nakagawa et al. (1983) data resulted in a better fit, with the average absolute error in calculated volumes being 0.07 cc/gmole.

For the three systems, aniline/benzene, aniline/chlorobenzene and aniline/ nitrobenzene compression (*k*) data were given by Gibson and Loeffler (1939a). They give parameters for the Tait equation (5-26) at 25° C and specified compositions of these three binaries. They claim that the Tait correlation is good over the pressure range of 1 to 1250 bars. Isothermal compressibility can be calculated by taking the derivative of the Tait equation and dividing by the volume, equation (5-27).

$$k = C_k \log_{10}\left(\frac{B_k + P}{B_k}\right) \tag*{(5-26}$$

$$\kappa_T = \frac{\log_{10}(e)\, C_k}{B_k + P} \tag*{(5-27}$$

where B_k and C_k are characteristic parameters. The isothermal compressibility was calculated at 1 bar for each condition given. These compressibilities were then fit to a quadratic equation in mole fraction for use in the DCFI database.

Thermodynamic Property Modeling

DCFI Modeling

If the DCFI are known, the activity coefficient and solution density can be calculated. This is incontrast to the usual situation where solution densities must be obtained from one theory and activity coefficients from another that may lead to inconsistencies. To calculate densities and activity coefficient properties, three DCFIs for each binary pair must be known (C_{11}, C_{12} and C_{22}). For modeling purposes, these quantities can be calculated from experimental data using equations (5-6), (5-7) and (5-8).

For modeling it appears logical to separate the binary DCFIs into an easily calculated ideal quantity and an excess term. Equations (5-9), (5-10) and (5-11) illustrate the ideal term. The excess term is simply the difference between the real and ideal quantities. Figure 5-1 illustrates the three real and ideal DCFIs for the carbon tetrachloride/acetonitrile system. It is desirable that the excess term be small. In this case the excess term is no greater than 20% of the real quantity. Equations (5-12), (5-13) and (5-14) show the terms that make up the excess DCFI. It is the sum of an activity coefficient derivative quantity and a complicated function of excess volume and excess compressibility.

Campanella (1984) assumed the excess volumetric term, f_{ij} (v^E, κ_T^E), should be small. Therefore, the total excess quantity $(1\text{-}C_{ij})^E$ would resemble the activity coefficient derivative term and could be modeled with one of the forms given in equations (5-15) through (5-17). Figures 5-2, 5-3 and 5-4 show the excess DCFIs for the same system, carbon tetrachloride/acetonitrile. It is clear from the figures that the f_{ij} (v^E, κ_T^E)'s are not insignificant. In fact, the excess volume term dominates the excess DCFI. This behavior has been found for many of the systems examined here. Also evident from the figures of excess DCFI is that they are not even symmetrical.

Empirical modeling of these excess quantities would be further complicated by the thermodynamic connections that require one model with the same parameters to describe all three excess functions. Also, while the $(1\text{-}C_{ii})^E$ quantities have constraints--they must be zero when x_i is equal to one--the cross term, $(1\text{-}C_{ij})^E$, has no such constraint. For all of these reasons, pursuing a modeling effort for excess DCFIs appears to be unpromising.

Activity Coefficient Modeling from DCFIs

Of primary interest in many phase equilibrium calculations is the activity coefficient. The composition derivative of the activity coefficient in a binary solution

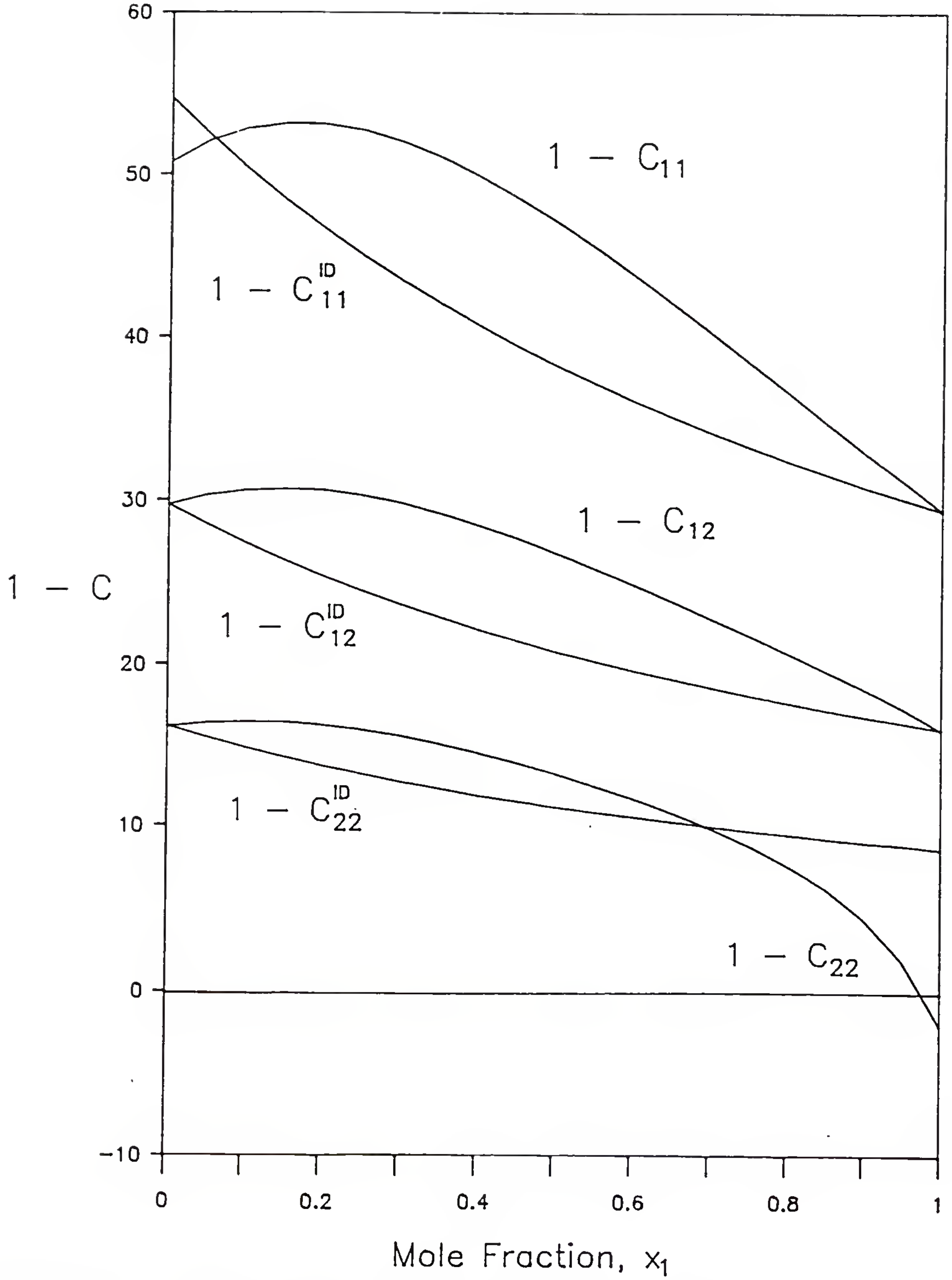

Figure 5-1 Real and Ideal Binary DCFIs for the System Carbon Tetrachloride(1) / Acetonitrile(2) Using Activity Coefficient Derivatives Calculated From VLE Data of Brown and Smith (1954) Fit to the Wilson Model.

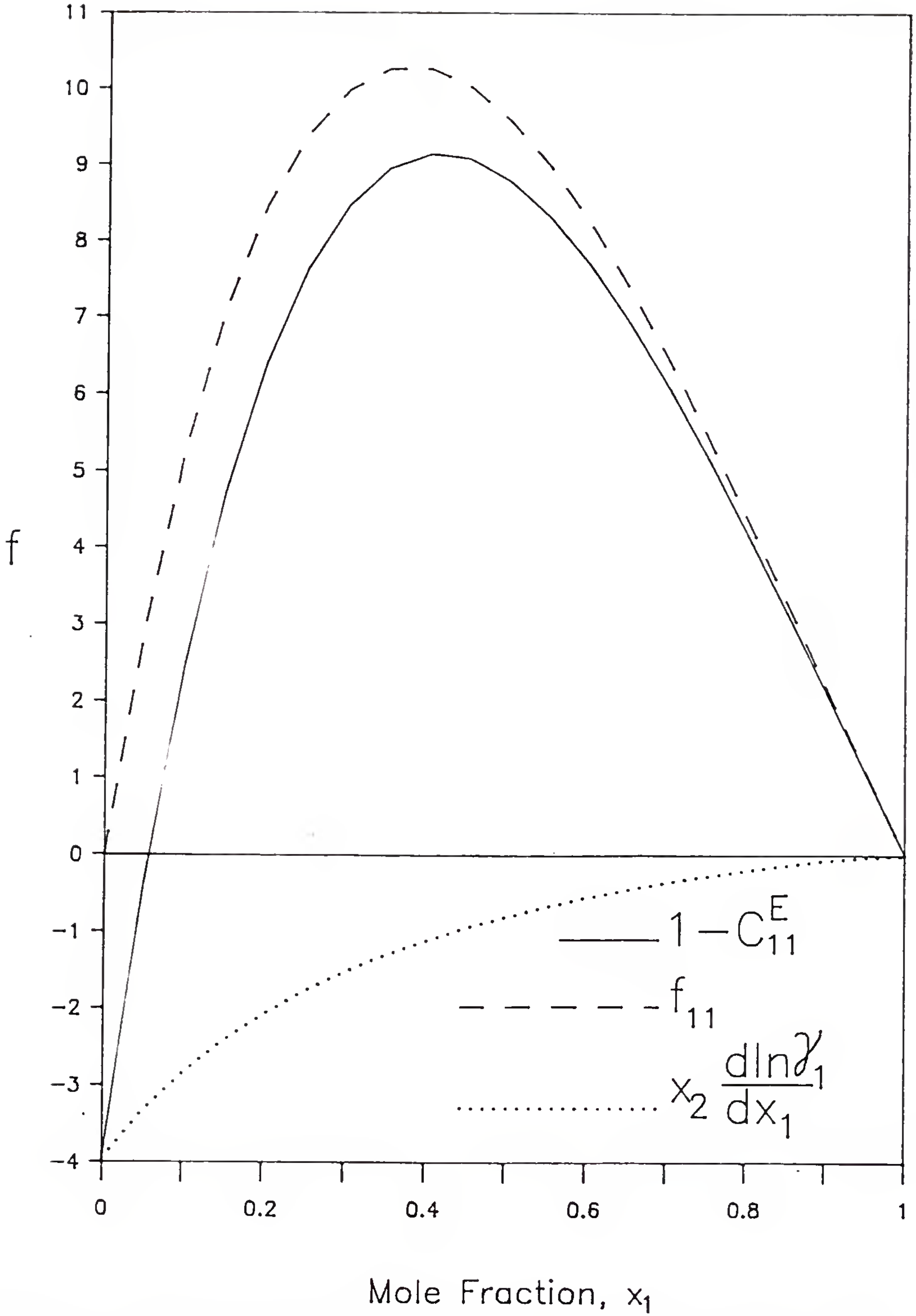

Figure 5-2 Excess DCFI $(1-C_{11})^E$ and Its Components; An Excess Volume Function, f_{11}, and the Activity Coefficient Derivative Term for the System Carbon Tetrachloride(1) / Acetonitrile(2). Calculated Using Activity Coefficient Derivatives From the VLE Data of Brown and Smith (1954) Fit to the Wilson Model.

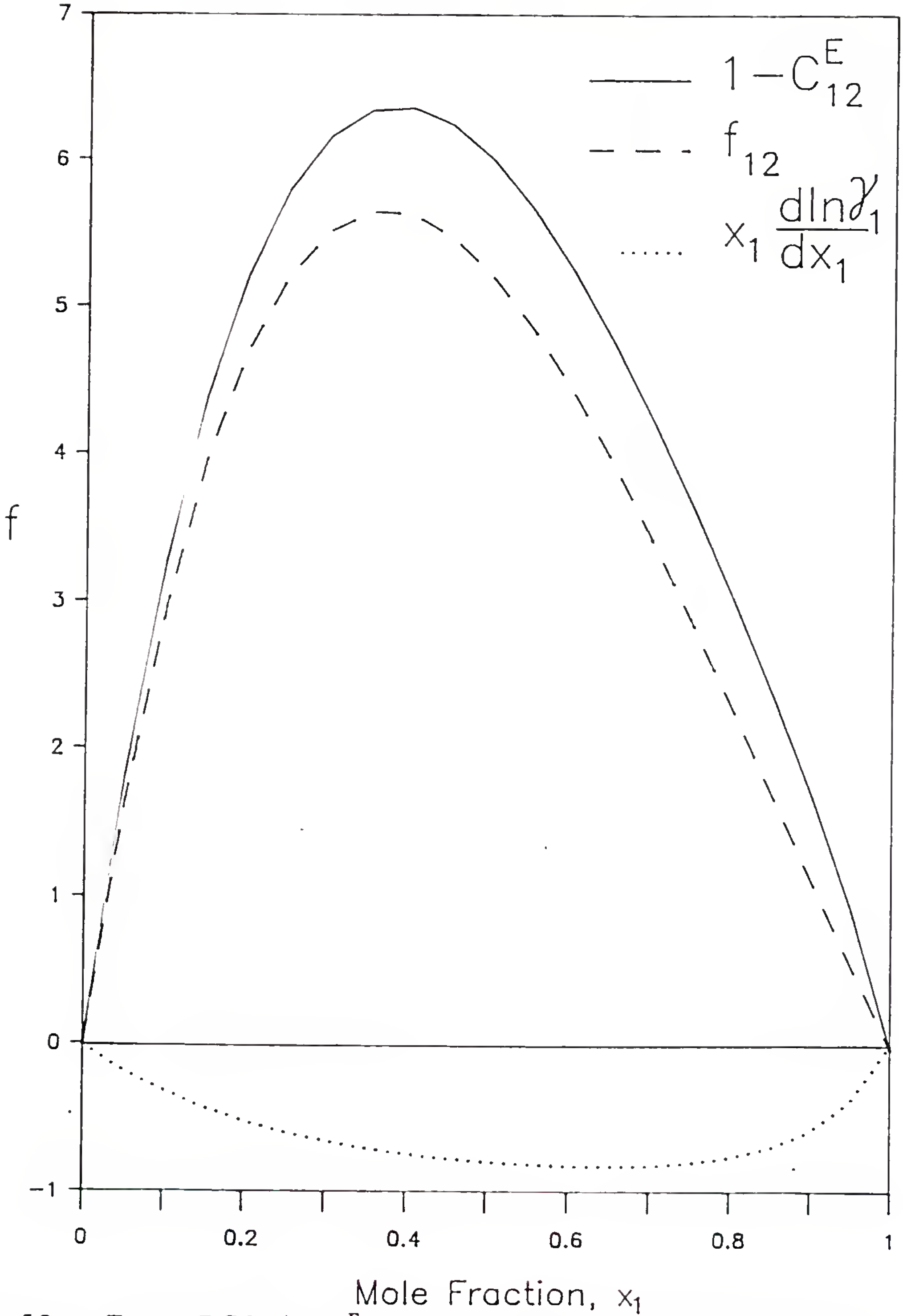

Figure 5-3 Excess DCFI $(1-C_{12})^E$ and Its Components; An Excess Volume Function, f_{12}, and the Activity Coefficient Derivative Term for the System Carbon Tetrachloride(1) / Acetonitrile(2). Calculated Using Activity Coefficient Derivatives From the VLE Data of Brown and Smith (1954) Fit to the Wilson Model.

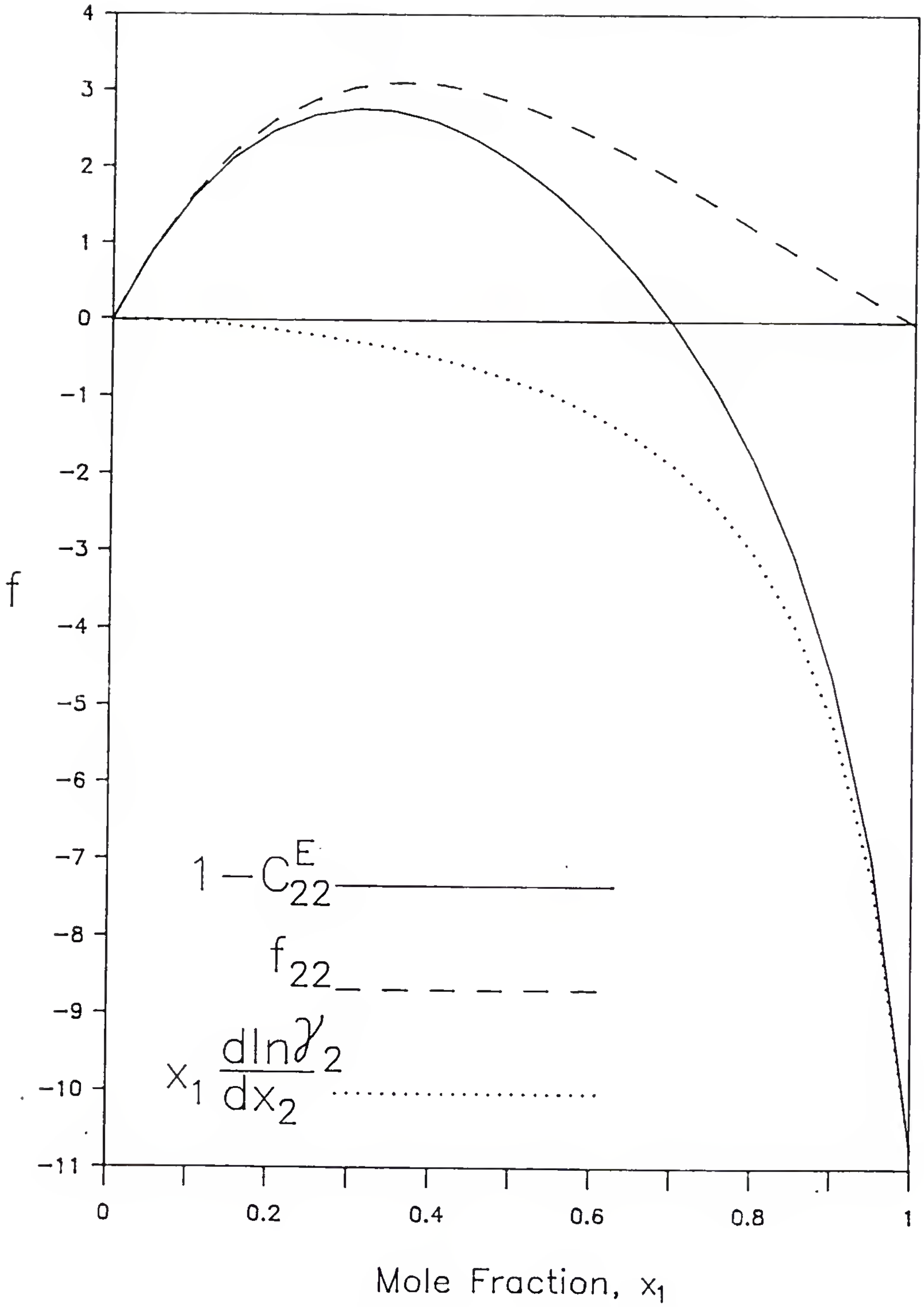

Figure 5-4 Excess DCFI $(1-C_{22})^E$ and Its Components; An Excess Volume Function, f_{22}, and the Activity Coefficient Derivative Term for the System Carbon Tetrachloride(1) / Acetonitrile(2). Calculated Using Activity Coefficient Derivatives From the VLE Data of Brown and Smith (1954) Fit to the Wilson Model.

can be written directly in terms of three pair DCFIs as in equation (5-18). Equation (5-18) is rewritten as equation (5-28)

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = x_2\,\Delta C\,/\,\chi \qquad (5\text{-}28$$

where χ is $1/\rho\,\kappa_T\,RT$ and ΔC is $[(1-C_{11})(1-C_{22})-(1-C_{12})^2]$. For modeling it would appear convenient to remove the bulk modulus (χ) and calculate it separately. However, the real mixture bulk modulus requires excess volume and mixture compressibility data to calculate. These data are not always available, nor should they be required for the calculation of activity coefficients. To retain the form of equation (5-28), without the requirement of needing mixture volume properties, the real bulk modulus is replaced with a more easily calculated ideal term.

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = x_2\,\Delta C^o\,/\,\chi^o \qquad (5\text{-}29$$

$$\text{where } \chi^o = 1\,/\,\rho^o\,\kappa_T^o\,RT = 1\,/\,\frac{(x_1\,V_1^o\,\kappa_{T1}^o + x_2\,V_2^o\,\kappa_{T2}^o)RT}{(x_1\,V_1^o + x_2\,V_2^o)^2} \qquad (5\text{-}30$$

This means that

$$\Delta C^o = \Delta C\,\chi\,/\,\chi^o \qquad (5\text{-}31$$

The quantity ΔC^o is somewhat less complicated than ΔC.

For modeling ΔC^o (calculated from the DCFI database) the form suggested by Campanella (1984) and shown in equations (5-15) through (5-17) is used. After examination of the ΔC^o for many systems it appeared that the inverse would be a better term to model for two reasons. First, many systems show a compositional variation of ΔC^o like that of Figure 5-5. The inverse of this, shown in Figure 5-6, is more well behaved. Secondly, the form for modeling suggested earlier is of an inverse polynomial. By modeling $1/\Delta C^o$, a polynomial model can be used.

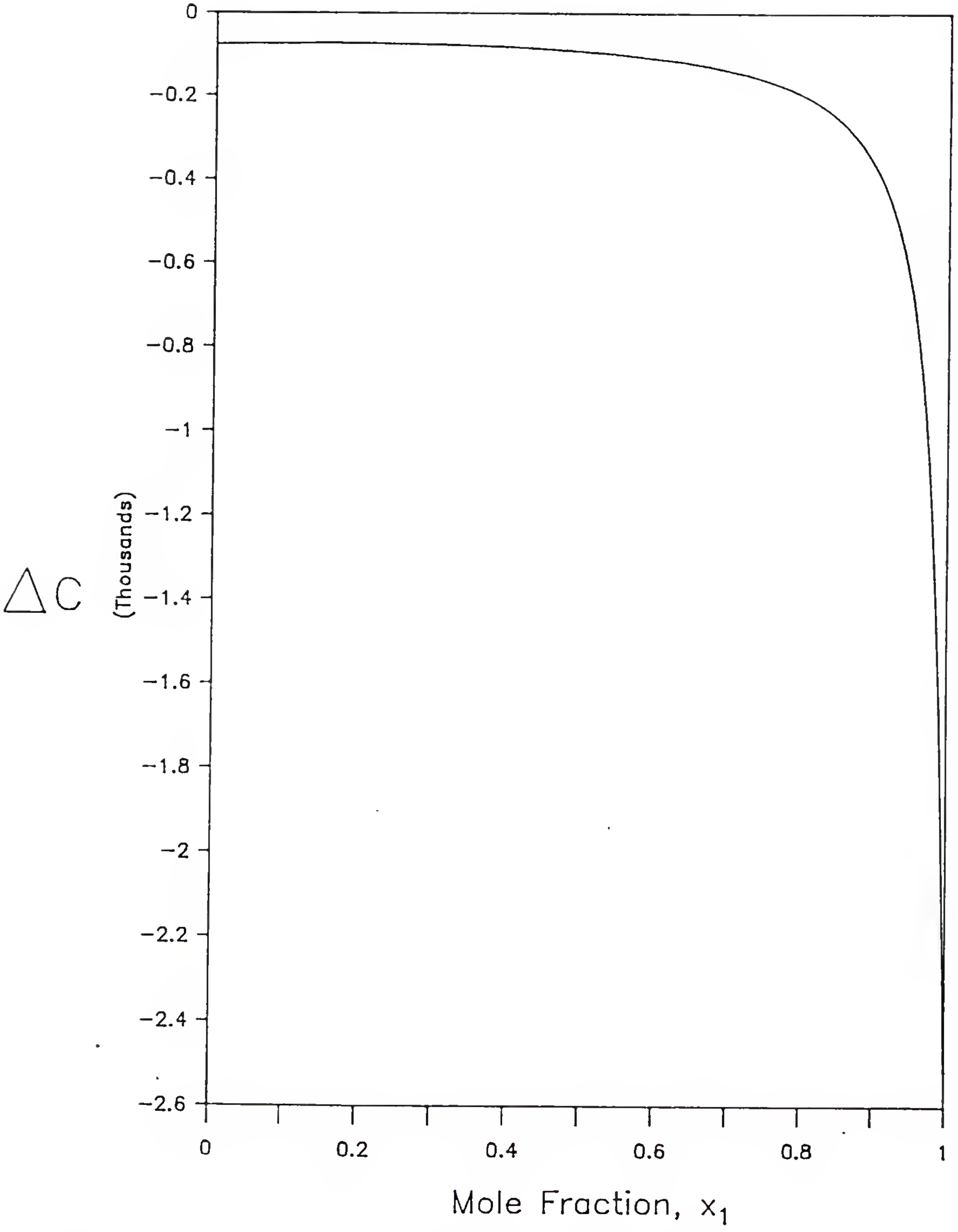

Figure 5-5 Combination of DCFIs, $[(1-C_{11})(1-C_{12})-(1-C_{22})^2)]$ or (ΔC) for the System Carbon Tetrachloride(1) / Methanol(2). Calculated Using Activity Coefficient Derivatives From VLE Data of Wolff and Hoppel (1968) fit to the Wilson Model.

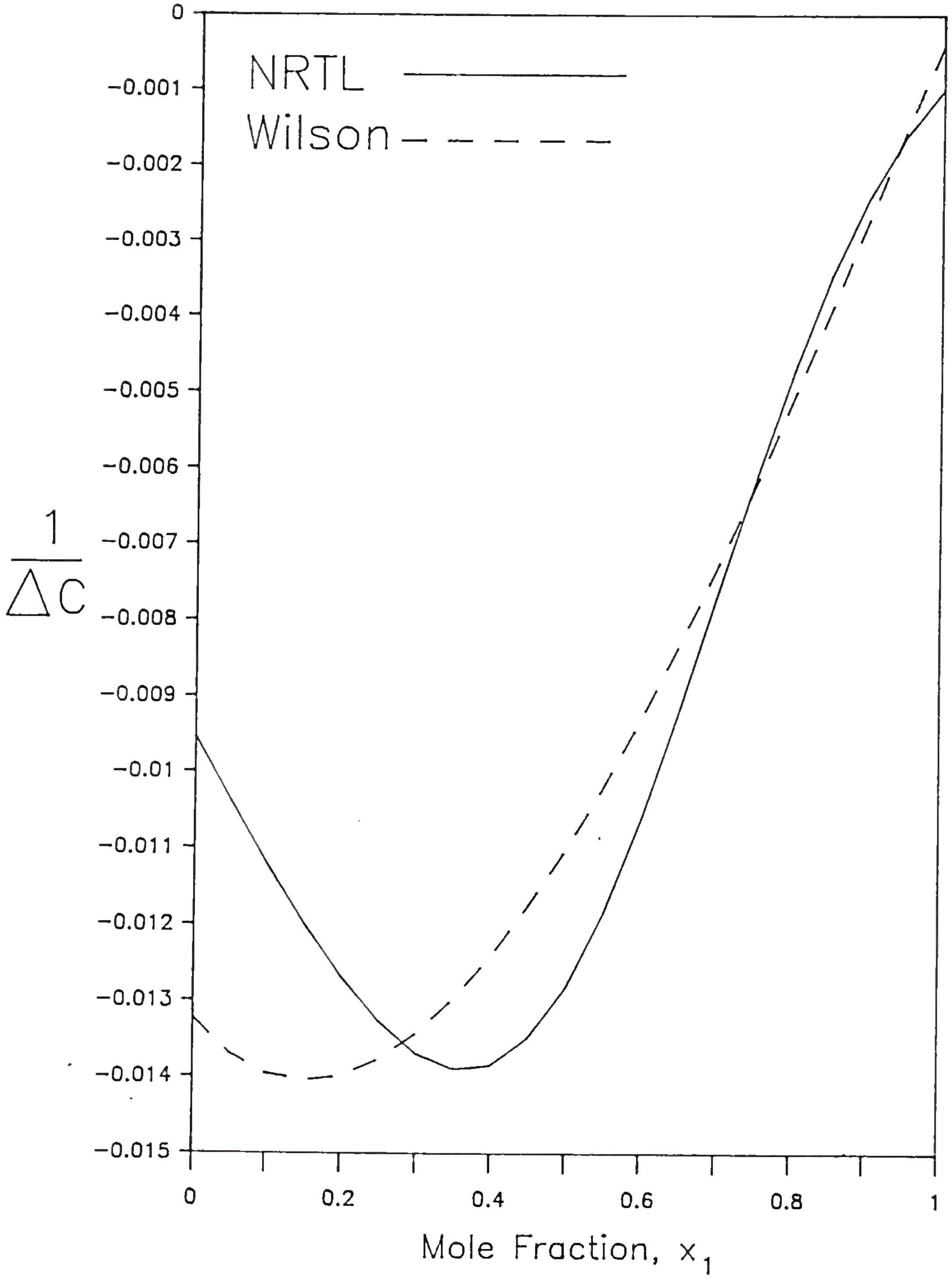

Figure 5-6 ΔC Inverse for the System Carbon Tetrachloride(1) / Methanol(2). Calculated Using Activity Coefficient Derivatives From VLE Data of Wolff and Hoppel (1968) Fit to the Wilson and NRTL Models.

Examination of values of $1/\Delta C^o$s for all of the systems in the data base pointed out four different types of compositional behavior, as shown in Figure 5-7. To simplify the screening efforts for new models, one system was chosen from each of these four groups. From group A, carbon tetrachloride/methanol, group B, methanol/water, group C, chloroform/ether and from group D, carbon tetrachloride/acetone. To model $1/\Delta C^o$, five equations were proposed

$$1/\Delta C^o = a_1 + b_1\, x_1 \qquad \text{(5-32a}$$

$$1/\Delta C^o = -(a_2 + b_2\, x_1)^2 \qquad \text{(5-32b}$$

$$1/\Delta C^o = (a_3 + b_3\, x_1)^3 \qquad \text{(5-32c}$$

$$1/\Delta C^o = a_4 + b_4\, x_1 + c_4\, x_1^2 \qquad \text{(5-32d}$$

$$1/\Delta C^o = a_5 + b_5\, x_1^2 \qquad \text{(5-32e}$$

As can be seen from Figure 5-7, two of the groups (B and D) are fairly simple, with no maxima or minima. They can be modeled well with the simple equation (5-32a). Equation (5-32d), because of its three parameters, fits all cases well. Some of the forms above are limited in the types of curvature they can describe. Equation (5-32b) will always have a negative second derivative, data from group B have a positive second derivative. Equation (5-32e) will always have first and second derivatives of the same sign, group D has first and second derivatives of opposite sign. For the simple forms of groups B and D, equation (5-32a) does an adequate job.

The other groups, A and C, both show extrema. The best fit to either of these is the three-parameter equation (5-32d). Figures 5-8 and 5-9 show the generalized least squares fit of some of the above models to data calculated from the database using the Wilson model for activity coefficient derivative data. Data calculated using the NRTL model for activity coefficient derivatives are also shown on the curves.

While there appear to be significant discrepancies between the data and the $1/\Delta C^o$ models, the activity coefficients calculated from these models by numerical

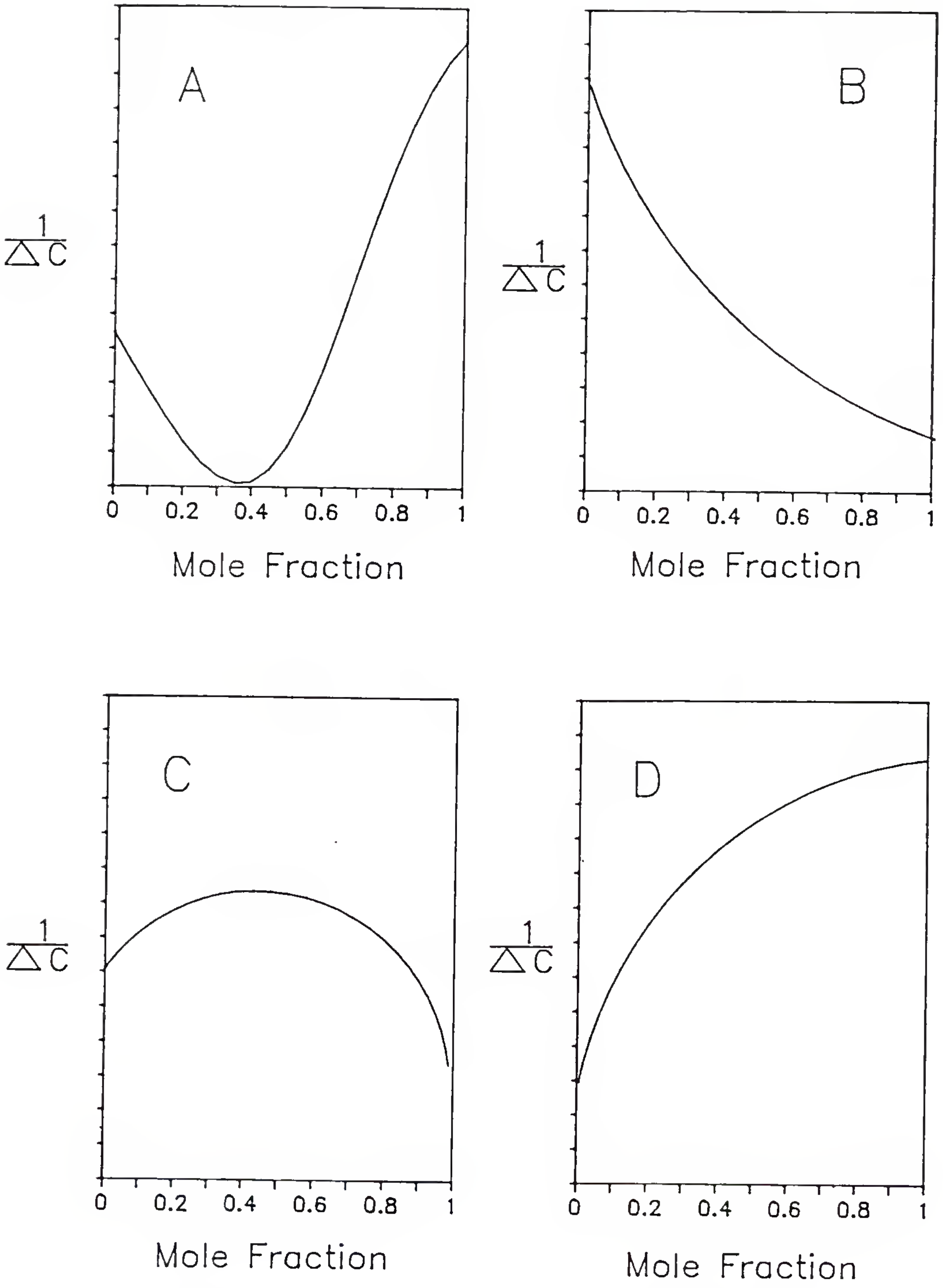

Figure 5-7 Four Characteristic Types of Compositional Behavior In 1 / ΔC.

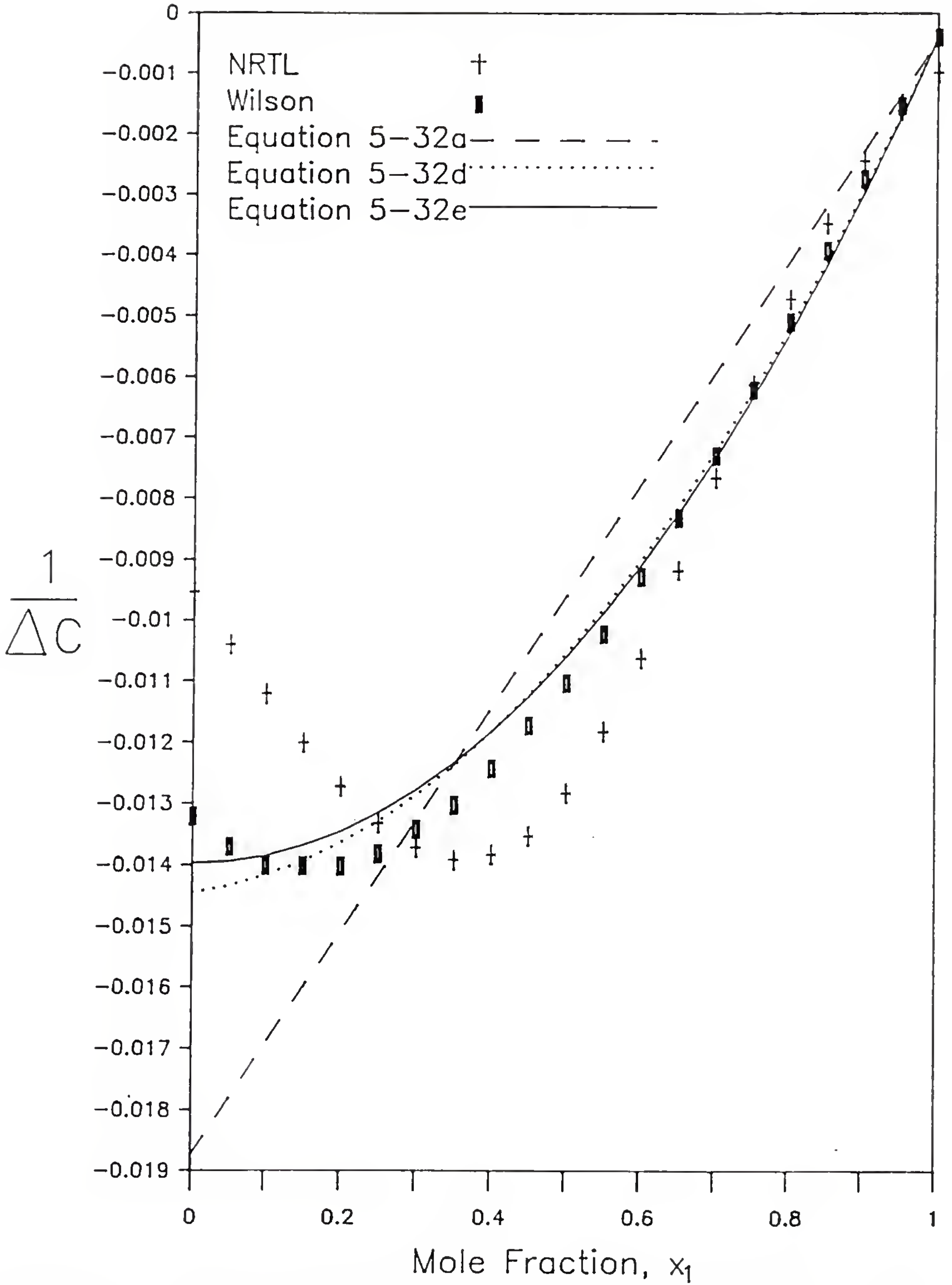

Figure 5-8 Generalized Least Squares Fit of Various Models to $1/\Delta C$ (Wilson) Data for the System Carbon Tetrachloride(1) / Methanol(2). $1 / \Delta C$ Data Calculated Using Activity Coefficient Derivatives From the VLE Data of Wolff and Hoppel (1968) Fit to the Wilson and NRTL Models.

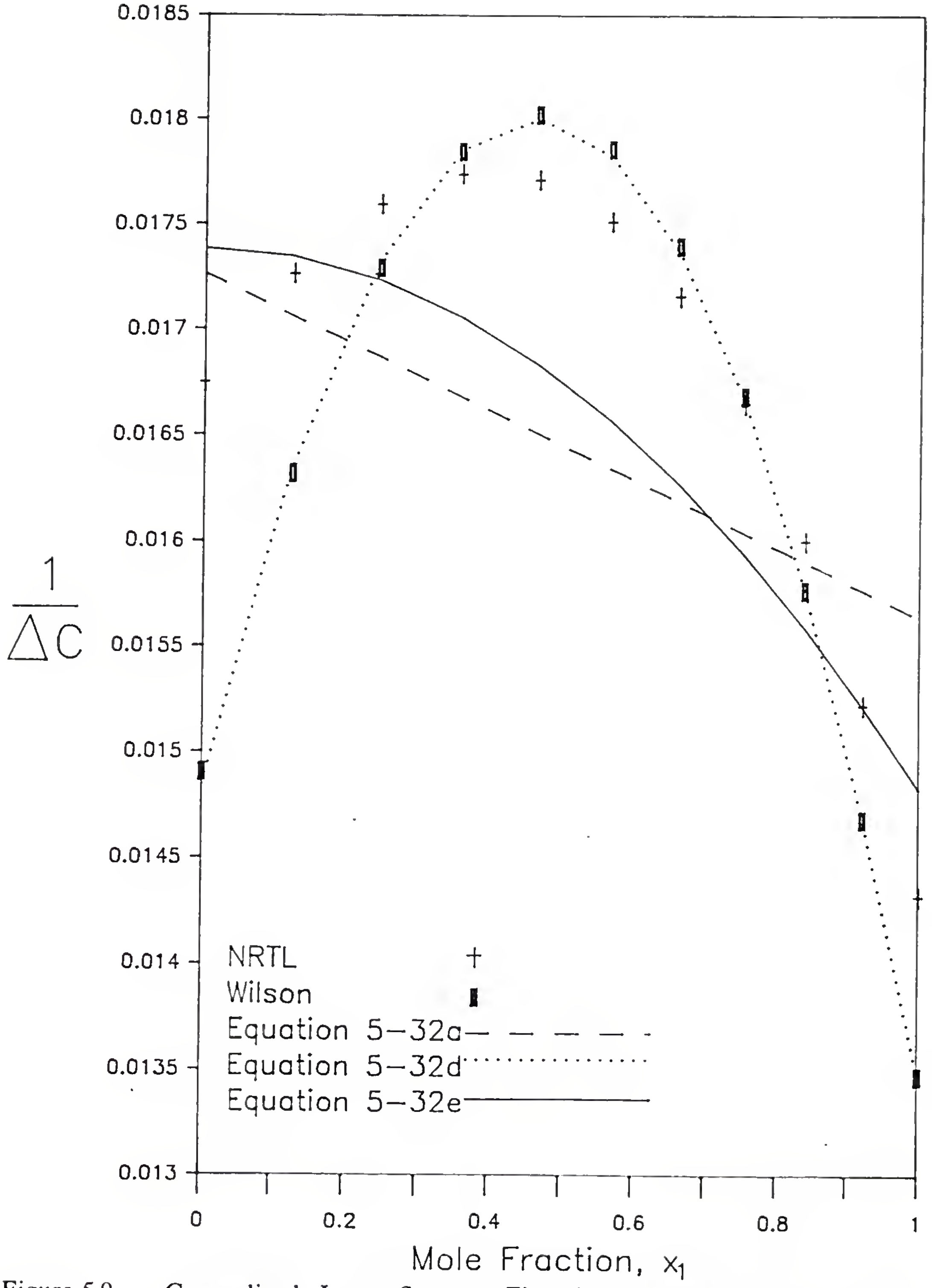

Figure 5-9 Generalized Least Squares Fit of Various Models to 1/ΔC (Wilson) Data for the System Chloroform(1) / Diethyl Ether(2). 1 / ΔC Data Calculated Using Activity Coefficient Derivatives From the VLE Data of Becker et al. (1974) Fit to the Wilson and NRTL Models.

integration of equation (5-33) are in reasonable agreement with data as shown in Figures 5-10 and 5-11.

$$\ln\gamma_1 = \int_1^{x_1} x_2\, \Delta C^o / \chi^o\, dx_1 \tag{5-33}$$

For the chloroform/diethyl ether system even a bad fit of the 1/ΔC° will calculate a reasonable activity coefficient as in Figure 5-10. This is because even the worst 1/ΔC° model misses the data no more than 15%. However, in the carbon tetrachloride/methanol case, even the three parameter model has a hard time fitting the 1/ΔC° data to within 15%. The result is a much poorer calculation of the activity coefficient as in Figure 5-11. However, this may not be typical; a different system from group A, carbon tetrachloride/acetonitrile, was less dramatic in its curvature and the models worked better. The alcohol systems are very difficult to model as is evidenced by the difference in the 1/ΔC°s when calculated from data based on the Wilson or the NRTL activity coefficient models.

Recalculation of activity coefficients from any of these models using numerical integration of equation (5-33) is straight forward. However, to be useful, an analytical form is needed to allow the model's parameters to be fit to VLE data. Equation (5-33) is complex due to the ideal bulk modulus term. Therefore, two additional forms of the bulk modulus term have been suggested

$$(1 / \chi_A^o) = (1 / \chi_1^o)\, x_1 + (1 / \chi_2^o)\, x_2 \tag{5-34}$$

$$(1 / \chi_B^o) = \frac{1}{\chi_1^o\, x_1 + \chi_2^o\, x_2} \tag{5-35}$$

Two new forms of the ΔC function appear along with these

$$\Delta C_A^o = \Delta C\, \chi / \chi_A^o \tag{5-36}$$

and

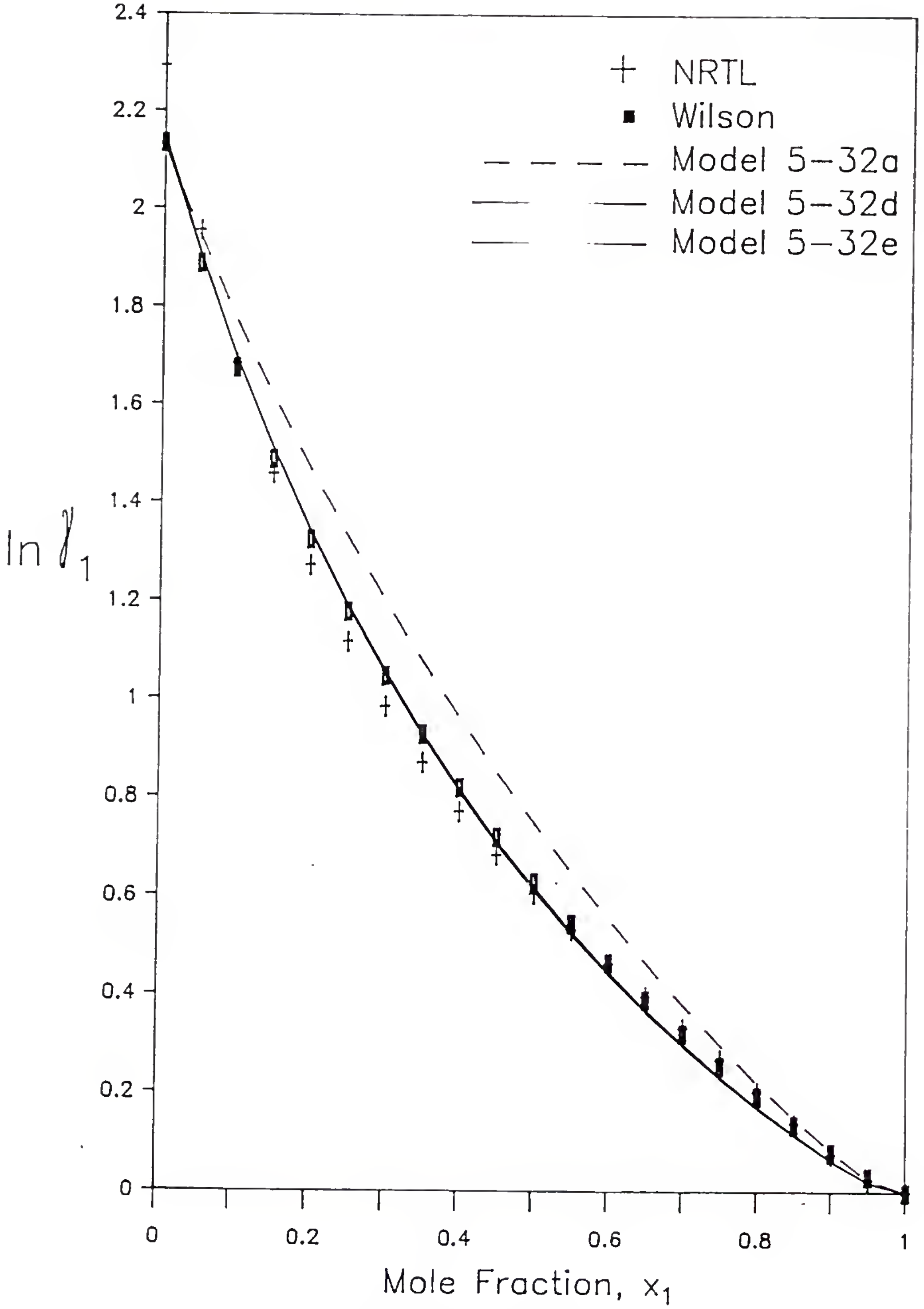

Figure 5-10 Activity Coefficient Data Calculated by Numerical Integration of Various Models Using Parameters Regressed to 1 / ΔC Data for the System Carbon Tetrachloride(1) / Methanol(2), Compared With VLE Data of Wolff and Hoeppel (1968) Fit to the Wilson and NRTL Models.

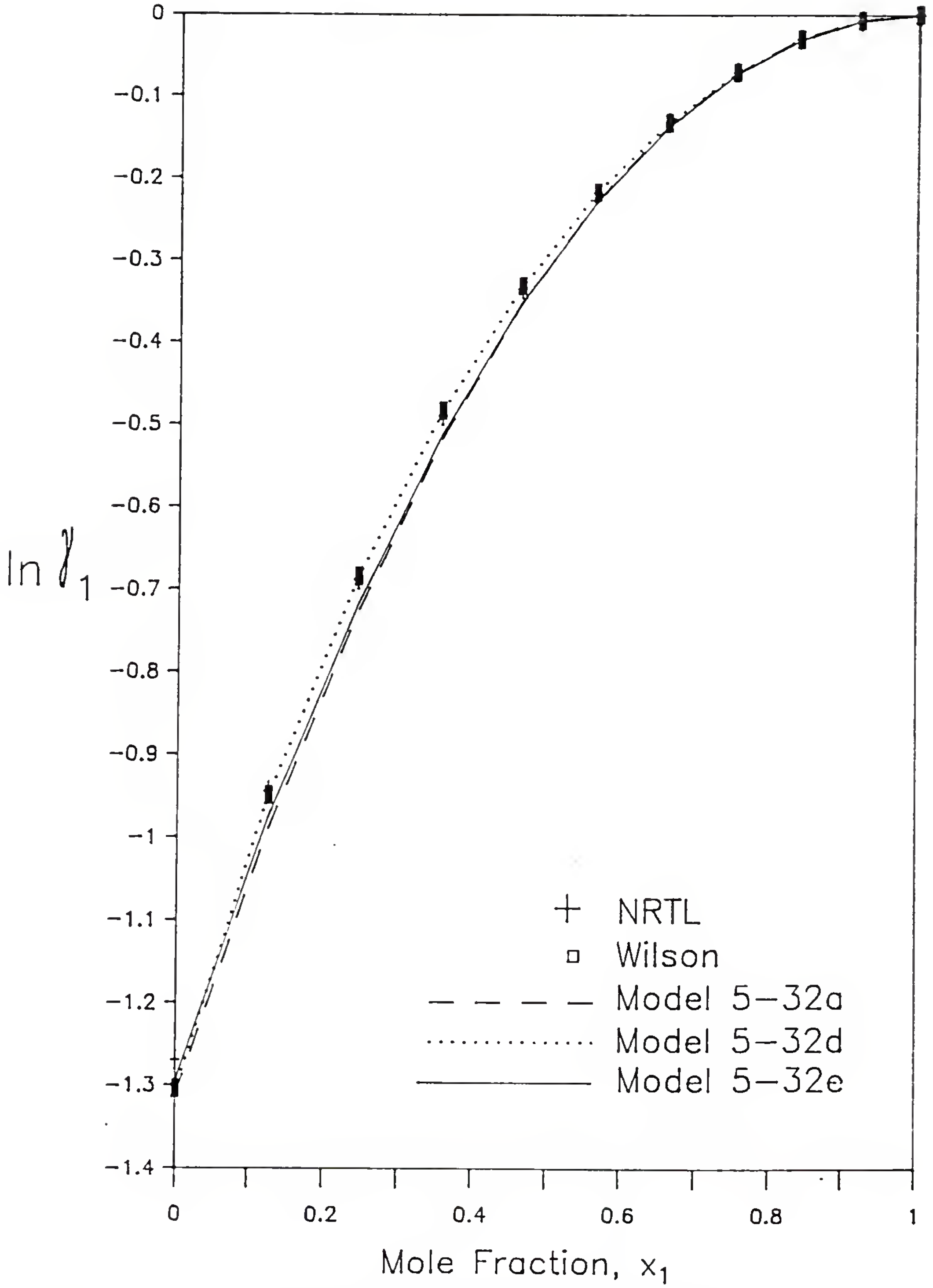

Figure 5-11 Activity Coefficient Data Calculated by Numerical Integration of Various Models Using Parameters Regressed to 1 / ΔC Data for the system Chloroform(1) / Diethylethyl Ether(2), Compared With VLE Data of Becker et al. (1974) Fit to the Wilson and NRTL Models.

$$\Delta C^o_B = \Delta C\ \chi\ /\ \chi^o_B$$ (5-37

These forms of ΔC are similar enough to the previous ΔC^o that equations (5-32a-e) fit them equally well or better. To develop an analytic activity coefficient, equation (5-35) was selected for the bulk modulus term and equation (5-32a) was selected for the $1/\Delta C^o_B$ term. Substituting equation (5-35) and (5-32a) into equation (5-33) results in the following activity coefficient equation

$$\ln\gamma_1 = \int_1^{X_1} \frac{1 - x_1}{(a + b\ x_1)\,(\Delta\chi^o\ x_1 + \chi^o_2)}\, dx_1$$ (5-38

$$\ln\gamma_1 = \frac{1}{a\Delta\chi^o - b\chi^o_2}\ \ln\left[\left(\frac{\chi^o_2 + \Delta\chi^o\ x_1}{\chi^o_1}\right)^C \left(\frac{a + b}{a + b\ x_1}\right)^{(1\ +\ a/b)}\right]$$ (5-39a

where, $C = 1 + \chi^o_2\ /\ \Delta\chi^o$

$$\ln\gamma_2 = \frac{1}{b\chi^o_2 - a\Delta\chi^o}\ \ln\left[\left(\frac{\chi^o_1 - \Delta\chi^o\ x_2}{\chi^o_2}\right)^D \left(\frac{a}{a + b - b\ x_2}\right)^{-\ a/b}\right]$$ (5-39b

where, $D = 1 - \chi^o_1\ /\ \Delta\chi^o$

and$\Delta\chi^o = \chi^o_1 - \chi^o_2$ and $\chi^o_i = 1\ /\ \rho^o_i\, \kappa^o_{Ti}\ RT$

All of the systems in the database have been fit to this equation, generally giving good results (see Appendix H for fitted parameter values). Figures 5-12 and 5-13 show the fit of this equation to the data from the Wilson activity coefficient model for the systems; carbon tetrachloride/methanol and chloroform/diethyl ether. The chloroform/diethyl ether shows an excellent fit, while the carbon tetrachloride/methanol fit is good, considering the difficulty that both the Wilson and NRTL models have fitting this system.

Summary

A database of DCFI's for 28 highly non-ideal systems has been assembled. The calculation of binary DCFIs requires mixture data of excess volume, vapor-liquid equilibria and isothermal compressibilities. For systems where low

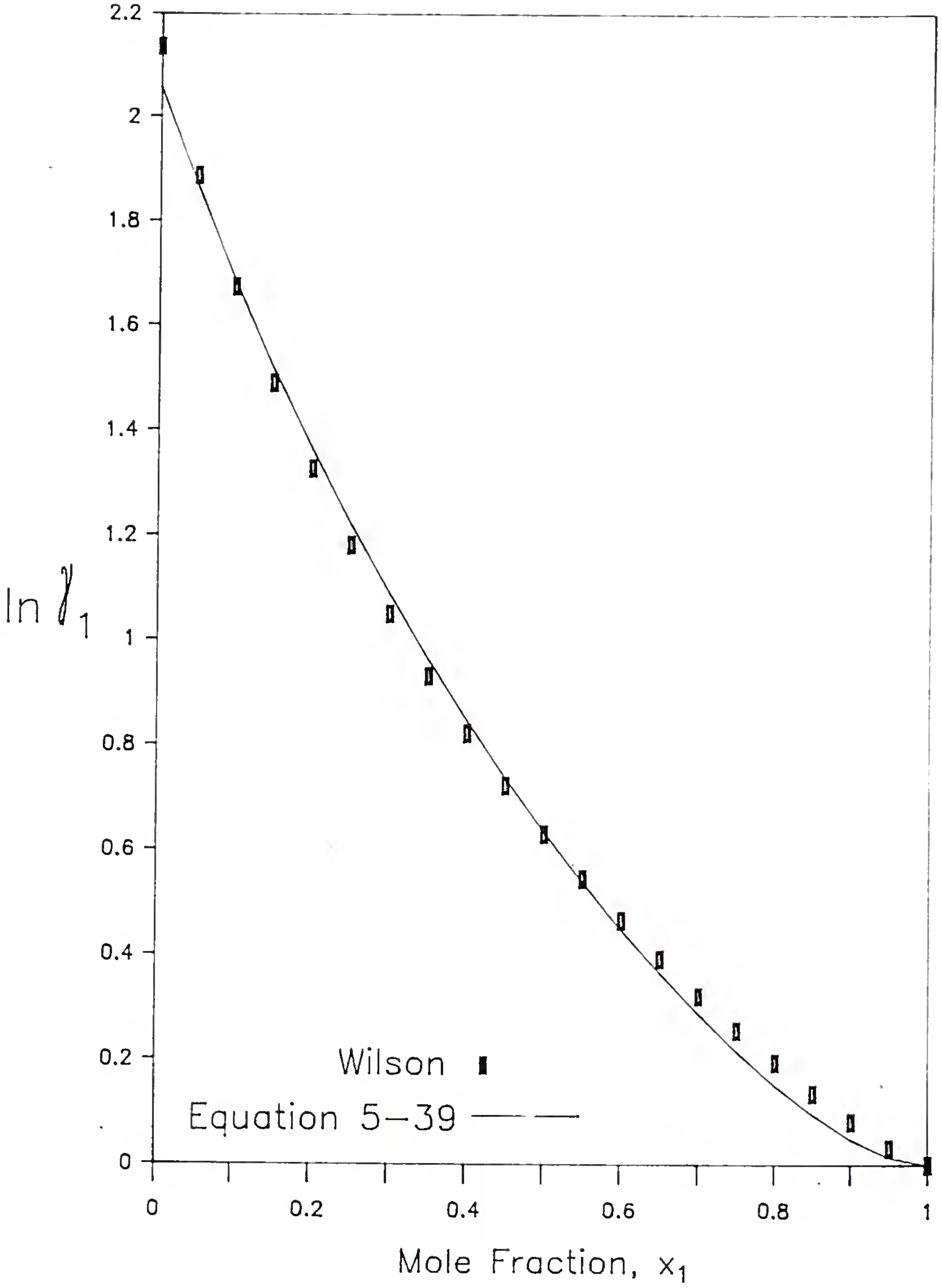

Figure 5-12 Activity Coefficient Data Calculated Using Eq. 5-39 for the System Carbon Tetrachloride(1) / Methanol(2), Using Parameters Regressed to Activity Coefficients From the VLE Data of Wolff and Hoeppel (1968) Fit to the Wilson Model.

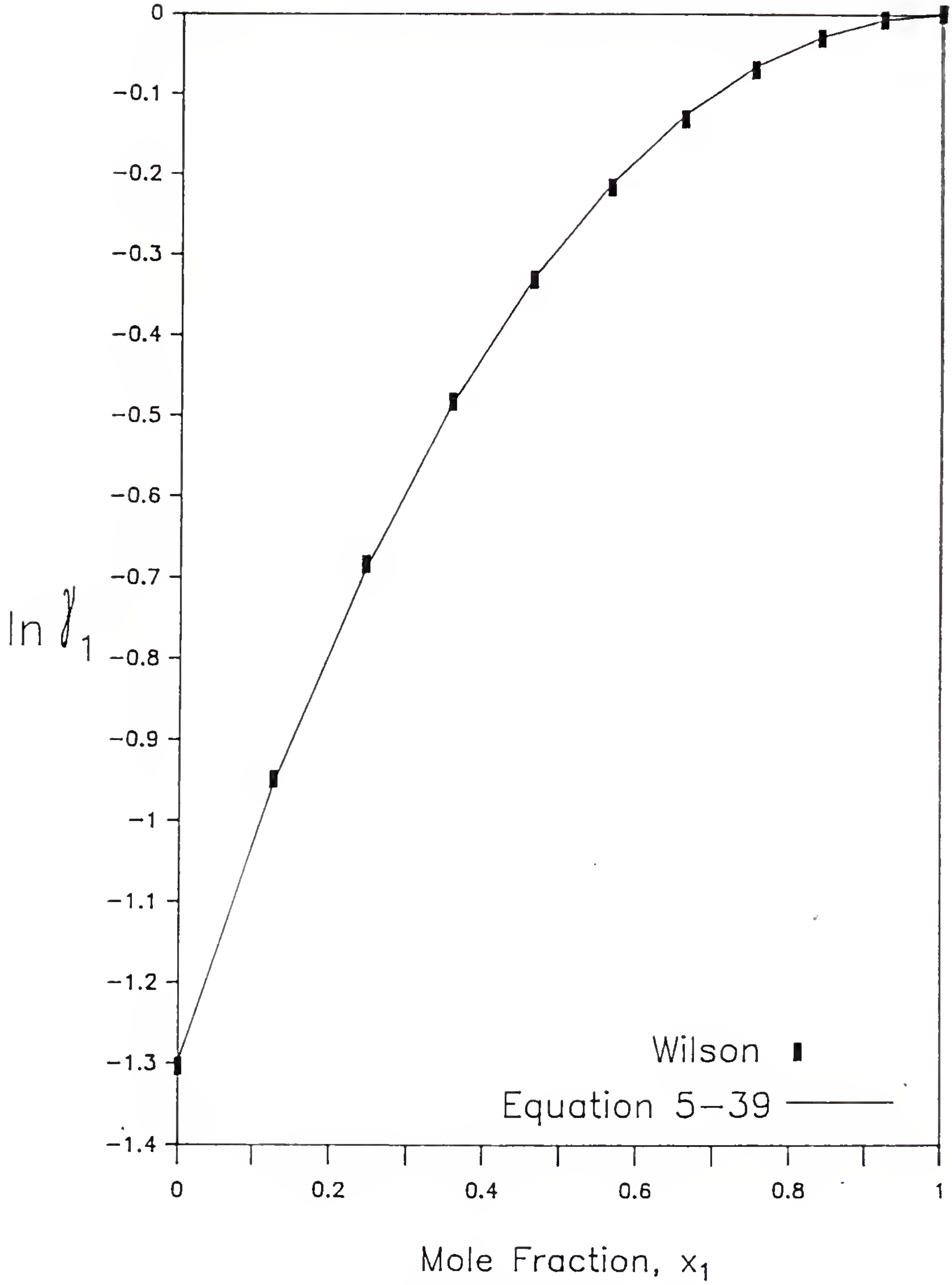

Figure 5-13 Activity Coefficient Data Calculated Using Eq. 5-39 for the System Chloroform(1) / Diethyl Ether(2), Using Parameters Regressed to Activity Coefficients From the VLE Data of Becker et al. (1974) Fit to the Wilson Model.

pressure mixture isothermal compressibility data were not available, Huang's (1986) liquid equation of state was used. Pure component and binary parameters have been found by fitting liquid PVT data.

An attempt to model individual DCFIs by use of an excess function proved unsuccessful because the difference between real and ideal DCFIs is usually dominated by the unsymmetrical excess volume term rather than the desired activity coefficient term. A second approach, by modeling only the activity coefficient with a grouping of DCFIs, has lead to a successful activity coefficient model for strongly non ideal binary systems.

CHAPTER 6

SUMMARY

Thermodynamic property models are an integral part of reliable process design. New models that are simple and rigorous are needed to describe new complex process technology (in areas such as bioprocessing and synfuels) and meet the demands of computer simulators. To meet this demand the fluctuation solution approach has been taken. Using this theory, thermodynamic property models in terms of the direct correlation function integrals (DCFI) are free of common simplifying assumptions. The solution fluctuation approach was chosen because Mathias and O'Connell (1979, 1981) found this theory describes systems containing dissolved gases quite well. Campanella (1984), however, was not as successful using this approach for condensed-phase systems. One of the problems Campanella had was accurately describing the compositional behavior of the DCFI in these systems, especially at low concentrations. To better understand the compositional behavior of the solution fluctuation DCFIs and develop a new empirical model for calculation of thermodynamic properties, a database of binary DCFIs was developed.

To generate a database, the DCFI can be calculated from the binary data of; partial molar volume, isothermal compressibility and composition derivatives of the activity coefficient. Data for the calculation of partial molar volumes is readily available in the literature. Mixture isothermal compressibility data were either found in the literature or calculated with the liquid equation of state developed by Huang (1986). Activity coefficient derivatives are usually calculated by differentiating a specific model, such as Wilson (1964) or NRTL (Renon and Prausnitz, 1968) whose parameters were fit to vapor-liquid equilibria data. As Campanella (1984) pointed out, the specific model chosen will greatly affect the calculated activity coefficient derivative. To avoid this problem two experimental methods for direct measurement of the activity coefficient derivative were explored.

Activity coefficient derivatives can be obtained by measuring the concentration fluctuations of a binary system with light scattering techniques. A typical organic system of interest, cyclohexane/benzene, for which all necessary data were available, was completely analyzed. Results of this analysis, for cyclohexane/benzene, (Δn = 0.07) follow the prediction of Miller and Lee (1973) that activity coefficients of systems with a low refractive index difference (less than 0.2) cannot be determined by light scattering. A complete error analysis of the procedure for calculating activity coefficient derivatives from experimental data indicated that they are quite sensitive to errors in the required auxiliary data. Thus, it appears that this is not a viable method for determination of activity coefficient derivatives in any system. It might be interesting to test the method with a system having $\Delta n > 0.2$ for which all the auxiliary properties are available in order to determine if there are any possibilities of using this technique. However, such a high refractive index difference requirement would severely limit the systems available for study.

Equilibrium sedimentation in an analytical ultracentrifuge was also studied for direct determination of activity coefficient derivatives. The equipment for this experiment was a Beckman Model E analytical ultracentrifuge. The standard composition detection system was modified with a laser light source to allow detection of the low molecular weight systems of interest. A complete thermodynamic analysis was performed describing the solute activity coefficient derivative in terms of the measurable quantities in the ultracentrifuge. An uncertainty analysis of the experiment pointed out that with reasonable care the activity coefficient derivative can be determined to within 10% at concentrations near 2% for significantly non ideal systems.

Not all binary systems of chemicals are amenable to the ultracentrifuge technique. There must be a moderate difference in refractive index of the pure components ($\Delta n > 0.06$), a sufficient tendency of the solute to sediment in the solvent, [$(M_1 - \rho\overline{V}_1) > 35$] and moderate non ideality ($\gamma_1^{\infty} > 2$). A thorough screening was conducted to select interesting systems that meet these criteria. Nine systems were chosen and equilibrium sedimentation measurements and supporting refractive index measurements were made on five of them.

Chemical potential derivatives measured in the ultracentrifuge for each of the five systems studied were lower than those calculated from VLE data. In each system a multiplicative factor would bring the results to within experimental error of the VLE curves. The factor was not the same for all systems, nor was it the same for all systems using an identical solvent. An investigation of pressure effects on the physical properties of the systems, caused by the large pressure gradient in the sample cells, showed an insufficient correction. Possible impurities in the chemicals also do not appear to be the cause.

Experiments were run at different temperatures for all five systems. The effects of temperature were generally within experimental uncertainties.

Accepting a constant multiplicative factor for the ultracentrifuge data gives results which generally support the low concentration extrapolations of two equations, Wilson and NRTL, applied to VLE measurements. However, it was not possible to differentiate a best model for the the prediction of activity coefficient derivatives from VLE data.

In lieu of having experimentally determined activity coefficient derivatives, literature vapor-liquid equilibria data fit to both the Wilson and NRTL models were used to calculated these derivatives. Equation of state parameters for calculation of isothermal compressibilities using literature pressure, volume and temperature data were regressed using generalized least squares and are reported for 24 pure components and 11 binary systems. A DCFI database of 28 significantly non ideal binary systems was then assembled. A new activity coefficient model based on the fluctuation solution DCFI was developed from this database. The resulting equation shows the ability to model very non ideal systems, such as the carbon tetrachloride/methanol system.

A first modeling approach, which modeled individual excess DCFIs (difference between the real DCFI and an ideal DCFI) was abandoned. These functions are dominated by the unsymmetrical excess volume term whose general form is unclear, rather than the activity coefficient term whose general form is known.

The second approach, was to model a group of DCFIs. Using fluctuation solution theory the activity coefficient derivative can be written as a combination of DCFIs (ΔC) and the bulk modulus ($\chi = \rho\ \kappa_T\ RT$). Examining the inverse ΔC ($1/\Delta C$) exposed its fairly simple mathematical form. Only four characteristic types of compositional behavior were found in the database for $1/\Delta C$. For modeling the bulk modulus, several functions of mole fraction and pure component properties were tested. None seemed to affect the modeling of ΔC, so the simplest form was chosen. Several models for $1/\Delta C$ were tested based on a form similar to that displayed by the derivative of all common activity coefficient models (Campanella, 1984). For many systems the resulting activity coefficients calculated by numerical integration of the modeled activity coefficient derivative were fairly insensitive to the form chosen for $1/\Delta C$. The simplest forms of $1/\Delta C$ and χ were then combined and integrated to obtain the resulting activity coefficient model. The parameters for this model were regressed to activity coefficient data calculated from VLE data for many systems with excellent results. A future study might include regressing this model directly to binary VLE. Some improvement might also be obtained by exploring other ΔC and χ functions.

With this large database of DCFIs now available, future efforts to model thermodynamic properties using empirical or theoretical forms of this theory can now be easily attempted.

APPENDIX A

ULTRACENTRIFUGE OPERATION

The Beckman Model E ultracentrifuge used in these experiments is a vintage piece of equipment. It was built with few electronics and is equipped with an old style mechanical speed control. Therefore, the operation of the machine is quite complicated and very manual. To make the user's job easier and to insure that no important steps in the operation are missed which might cause a safety problem or harm the machine, the following procedure has been developed. This procedure offers the user a simple step-by-step set of instructions for efficient use of the Model E ultracentrifuge.

The first section of the procedure outlines the proper procedure for filling, emptying and cleaning of the cell. The second section, gives the actual operating procedure for the machine.

Assembly of Cell

1. Put white vinylite gasket in bottom of each window holder.
2. Clean windows with lens paper.
3. Place windows in holders with arrows pointing down, into holder (that will be pointing out of the cell when finally assembled) and align arrow with keyway in outside of holder. Use a piece of lens paper, do not touch the window surface directly!
4. Slip a white teflon window liner (non-Beckman part) into the space between the window and the holder. Put it in so ends are away from the keyway.
5. Be sure that all surfaces and the inside of the cell are clean. Stack the centerpiece

parts on the table with a window on the bottom, red polyethylene gasket (seat gasket under retaining lip with bevel-tipped plastic or wooden tool), centerpiece, red polyethylene gasket, other window. Place:

a. all serial numbers upside down,
b. both windows facing each other,
c. keyways aligned.

6. Remove the filling plug from the housing and push the cell housing down over the stack.
7. Turn the assembly over, holding the parts in with your finger, and slide the parts to the bottom, do not actually touch the window.
8. Apply a small amount of 'Spinkote' to the brown bakelite screw-ring gasket and place it on top of the upper window holder.
9. Lubricate the threads lightly (Spinkote) and insert screw-ring with "B" facing up.
10. Tighten finger tight.
11. Tighten with torque wrench. Place cell, with screw-ring up, in chuck and tighten lightly, align slot in screw-ring with wrench and lower cell into chuck, all the way to the bottom. Tighten chuck with cross bar and torque wrench to about 110 in. lb., and then torque the cell to 100 in. lb.
12. Fill cell using a syringe. Hold cell with filling hole pointing straight up, fill centerpiece with single quick motion of the plunger to bow the meniscus and push the air out, jiggling the needle at the hole slightly in the hole to let the air escape.

    CAUTION: Be careful not to scratch the cell in any way!

    If the cell overfills, blot out the excess in the fill hole.
13. Place a red polyethylene fill hole gasket in hole, screw plug in snug-tight.
14. Repeat 12 and 13 for reference cell.

Weigh and Assemble the Counter Balance

15. Select a brass or aluminum weight to bring the counter balance to within 0.5 grams of the filled cell weight, use the 0.5 gram weight if necessary.

    If the counter balance and cell cannot be the same weight, make the counter balance no more than 0.5 grams lighter, not heavier!

16. Screw the selected weight all the way into the counter balance from the top (the end with the small screw in it). If the 0.5 gram weight is being used, screw it in from the bottom, making it flush. It is important that the weight not protrude from the hole.

Loading Cell and Counter Balance into Rotor

17. With the rotor on its stand make sure the cell holes are perfectly clean.

18. Put a light coat of 'Spinkote' on the sides of the holes, insert cell in hole #1, screw-ring up, fill screws facing the center. Insert counter balance in hole #2, small screw up, and small screw headed to the left when looking toward the center of the rotor.

19. Align cell and counter balance in holes by matching the lines on the bottom of the rotor with those on the cell and counter balance. Use a small mirror on the table.

    Turn the counter balance with a screw driver.

    Turn the cell with the alignment tool.

20. Tighten the small screw on the top of the counter balance to secure in place.

Emptying and Cleaning the Cell and Holder

21. Push the cell out of the rotor with your finger.

22. Unscrew plug, remove screw plug gasket and discard.

23. Empty the cell with a syringe, being very careful not to scratch the interior of the cell.

24. Loosen the screw-ring with the torque wrench.

25. Unscrew screw-ring and remove the brown gasket, push the other parts out of the housing.

    Note: If the centerpiece doesn't come out easily, cool it in the refrigerator and then warm the holder in your hand, it should fall out.

26. Remove the red gaskets with a plastic tool and discard.
27. Wipe the windows dry with lens paper, if solvent has leaked around the windows, remove them from the holders and clean.
28. Soak the centerpiece and window holders, if necessary, in a 1% solution of mild non-alkaline soap. They can be scrubbed with pipe cleaners if necessary. Do not allow the wire to scratch either cell or window.
29. Soak the centerpiece and windows in hot deionized water for 10 minutes. Rinse in deionized water and blow dry.
30. Dry all other gaskets, examine and replace if worn.

Making a Run

Loading Rotor

1. Turn on MAIN POWER at Switch Box.
2. Make sure area UNDER Vacuum Chamber is CLEAR.
3. Lower Chamber. When chamber is fully opened, put hoist switch to SAFE.
4. Check to be sure Interference Light Limiting Slit is mounted on the support fork.
5. Check the Mercury Cup to see that it looks clean (use a Mirror) and that there is a film of silicone oil covering the mercury. This can be checked by placing a strip of paper in the cup, the oil will wet the paper.

   For the first run with a rotor:

   a. Pull the mercury cup up to it's highest position.
   b. Put plastic spacer ring on rotor.
   c. Install Rotor per step 7.
   d. Close chamber completely.

e. Open chamber and remove spacer.

This will have positioned the cup properly.

6. Check the needle on the bottom of the rotor. Feel it to make sure it has a smooth point. If it doesn't, REPLACE IT!
7. Attach ROTOR to drive shaft.
    a. Slide coupling nut up the drive shaft as far as it will go, about 1/2".
    b. Place the rotor in the chamber, with needle protector still in place, rest the rotor on the support fork.
    c. Lower the coupling nut and screw it clockwise until it engages.
    d. Turn the coupling nut until it's flat sides are parallel to the sides of the fork.
    e. Slide the coupling WRENCH over the coupling nut and support fork with the jaws of the wrench down.
    f. Hold rotor with both hands and turn it COUNTER-CLOCKWISE until it is SNUG TIGHT.
8. REMOVE COUPLING WRENCH FROM THE VACUUM CHAMBER!
9. Make sure the rotor clears the support fork equally on both sides.
10. Remove rotor needle protector from the rotor, do not hit the needle.
11. Put a light film of vacuum grease on the O-ring on top of the chamber.
12. Make sure the rotor needle protector, coupling wrench and spacer ring are out of the chamber, i.e., account for the location of each!
13. Close the chamber, return the hoist switch to SAFE.

Vacuum Pump

14. If vacuum gauge is not on zero, adjust it with the screw on its face.
15. CLOSE the air valve inlet to the chamber, and align slit with the vacuum pump switch. TURN VACUUM PUMP ON.

16. Turn on vacuum gauge, wait 2 minutes for the gauge to warm up, align the needle with the heavy line on the right side of the gauge using the vacuum gauge adjustment in the center of the control panel.

Refrigeration and Temperature Control

17. Turn on refrigeration. Switch is near the chamber hoist switch. The pilot light should come on.
18. Determine the refrigeration setting from the nomograph supplied with the centrifuge.
19. To set the refrigeration, remove the cap on the pressure gauge. This is located inside the unit, to the left of the vacuum pump. Turn the screw counterclockwise to reduce the temperature; one turn is about 6° F.
20. Recheck the gauge several minutes after setting the refrigeration to be sure it is still correct.
21. Turn the temperature control switch to ZERO ADJUST. The temperature pilot light should come on.
22. Wait 2 minutes for the unit to warm up. Then zero the black needle on the center line of the control dial with the zero adjust.
23. Set the RANGE and BALANCE knobs, per the previous calibration of the current rotor.
24. Move the red pointer to zero with the little knob in the center of the dial.
25. Turn the control switch to REGULATE.

To Indicate Temperature Only

26. Zero the black needle per step 22.
27. Switch to INDICATE and balance needle (use calibration chart, Figure A-1, to read temperature).

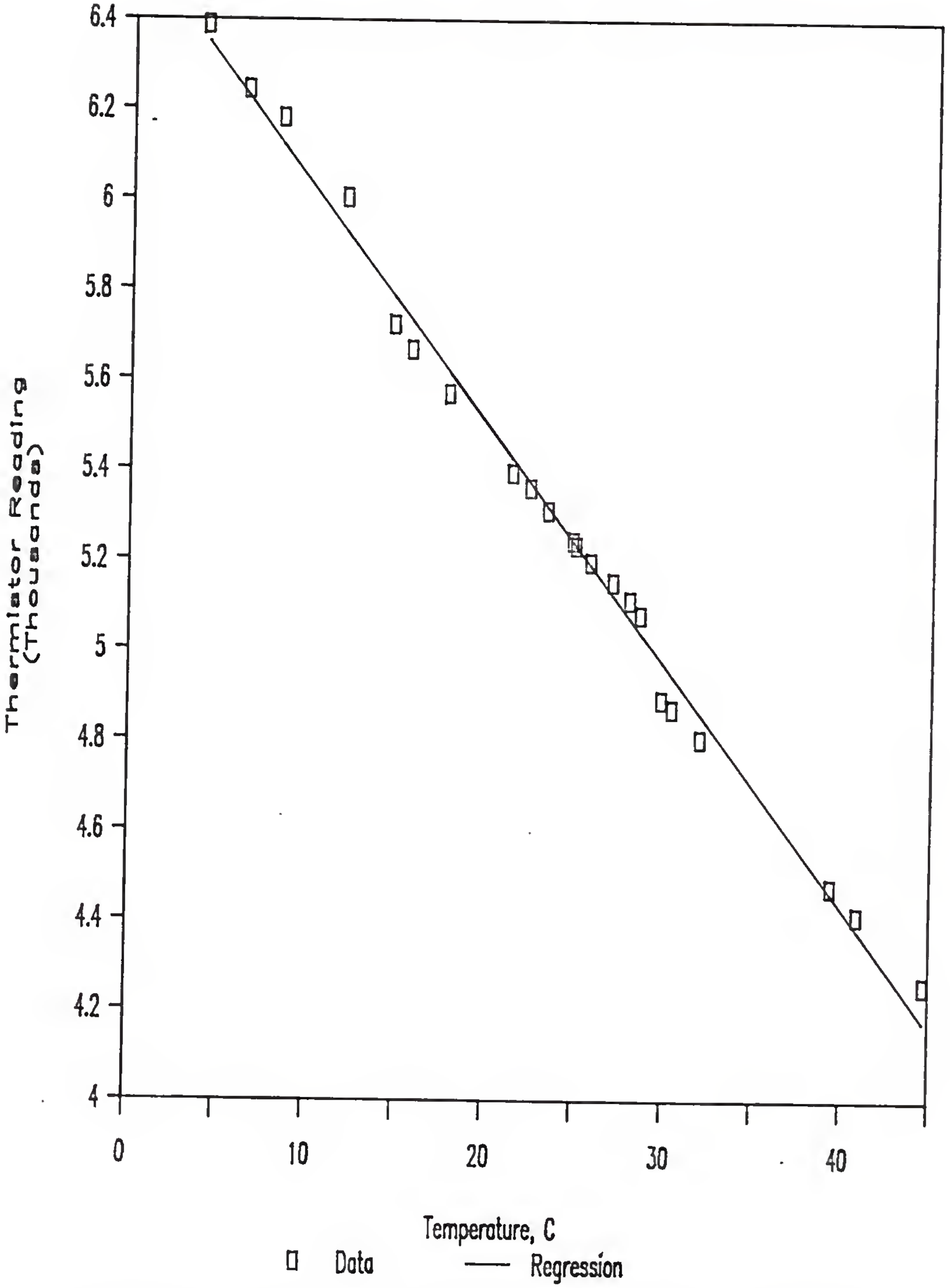

Figure A-1 Thermistor Calibration, Model E Ultracentrifuge Rotor, Model AN-D, Serial No. 3581. Calibrated November, 1986.

Diffusion Pump

28. Open the diffusion pump's water valve. (This also controls the cooling water to the drive unit.)
29. Check the drain to be sure water is flowing!
30. When the vacuum gauge needle pulls away from the right side of the gauge, turn on the DIFFUSION PUMP. The pilot light should come on to turn it off.
31. If the diffusion pump pilot light doesn't come on, check the Voltage Control, it must be OFF, turn it counterclockwise.

Laser Light

32. Turn switch on laser power supply to ON.
33. Remove covers from the two 45° mirrors.

Acceleration

Rotor Speed

Note: If the sample is denser than 1.2 g/cc, derate the square of the maximum speed in proportion to the increase in density, i.e., if $\rho = 0.2$ then the maximum speed is given by:

$$[(\text{OLD MAX})^2 / (2/1.2)]^{1/2}$$

Derate rotor 10% for every 1000 hours at maximum speed or every 1000 runs.

34. Set HI-LO knob to HI, this is the right hand speed scale.
35. Set the RANGE KNOB (to the left of the speed scale) to a range that contains the desired speed.
36. Set the speed selector arrow with the right knob to the desired speed.
37. Make sure the Voltage Control Knob is at its extreme counterclockwise position.
38. Set the Run Timer to the desired length of run, for runs longer than 5 hours set the timer to HOLD. The rotor will automatically brake when the timer reaches zero or is moved to zero manually.

39. Set the braking switch to SLOW, this is very important as damage can occur if the rotor is started with the switch not in SLOW.
40. Check that:
    a. Vacuum and Diffusion Pumps are on,
    b. Oil level is between the marks on the drive,
    c. Cooling water is flowing,
    d. Coupling wrench is out of the chamber.
41. Pull the view window out (which should be protected from direct laser light by crossed polarizers) and observe the light source and the amp meter as the voltage is slowly increased to a reading of 4 amps. The light should begin to flash, indicating that the rotor is spinning. If the light doesn't flash, STOP, something must be in the chamber.
42. If all is well, increase the voltage until the amp meter reads 14-15 amps. Do not exceed 15 amps or a fuse will blow.
43. Check the viewer again, if the rotor was loose and dropped off onto the fork there will be no light, or if the vacuum gauge goes up, there might be a leak in the cell. Switch the brake to RAPID and turn the timer to zero. Check for problems and start over.
44. As the rotor picks up speed the amperage will drop, keep turning the voltage control up until the approximate value needed for the desired speed is obtained (see Figure A-2). Do not let the amperage exceed 14 amps.
45. Continue checking the vacuum gauge, if there is a leak in the cell it will show up here. If so, SHUT DOWN!
46. When the Tachometer shows a speed within 1000 rpm of the desired speed, turn the voltage back to the value required for that speed. The required voltage can be estimated from the attached Figure A-2 or from previous experience.

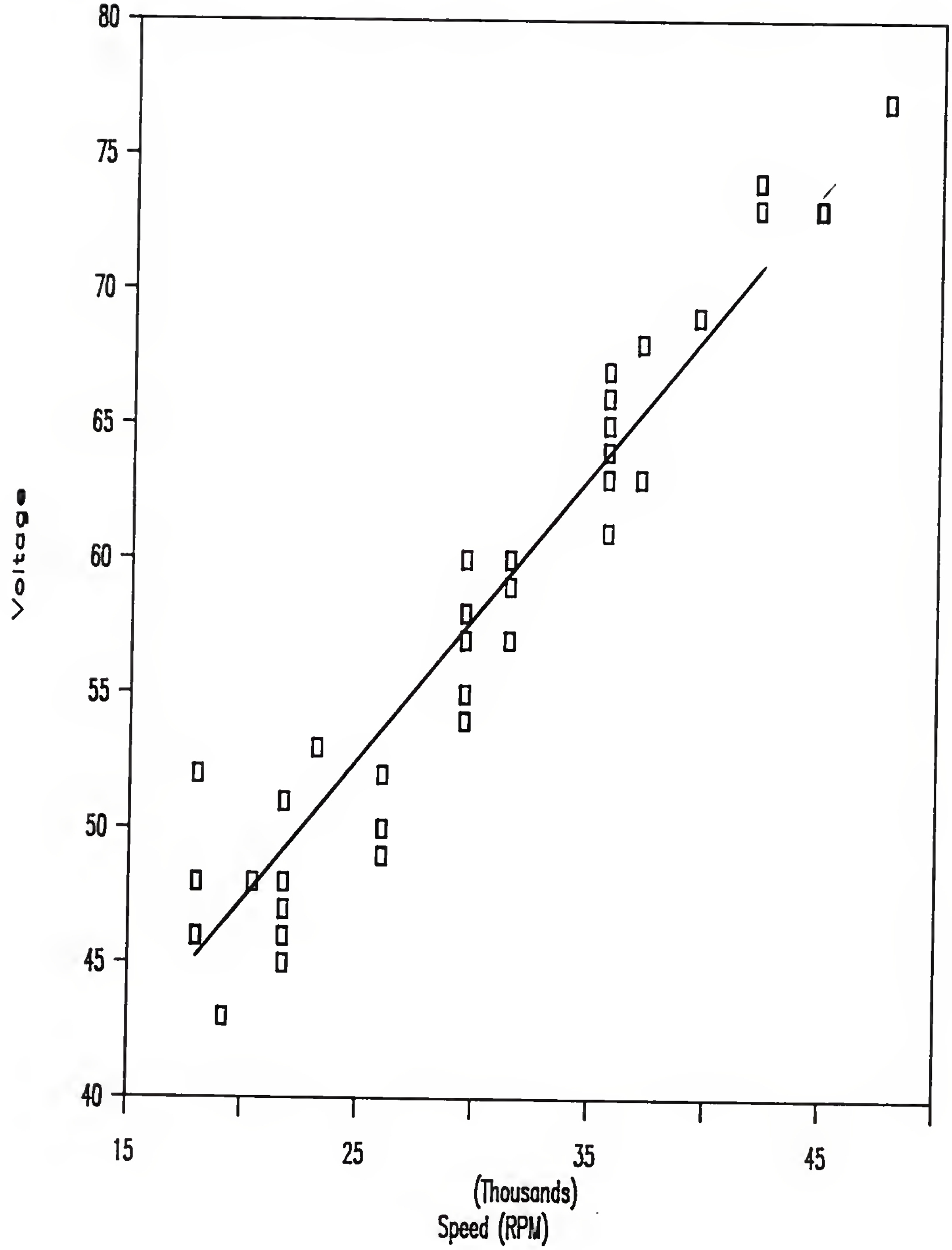

Figure A-2 Drive Voltage as a Function of Rotational Speed. Included are Data From Two Drives, and Two Different Cells.

47. When the rotor comes up to speed the left pilot light will go out. If it over speeds the right light will come on. If that happens, turn the voltage down 4 volts. If the accelerate light comes on again very quickly, increase the voltage a bit.

48. If the rotor over speeds too far the brake light will come on, wait until it goes out and then turn the voltage down. Try to avoid having this light come on.

    NOTE: When the voltage is correct, all three lights will be out and the ammeter needle will move sightly as the unit finely controls the rotor speed. Take note of the exact voltage for reference in starting up next time.

49. Once at operating speed, set the braking rate to RAPID.

50. Note the time and Odometer reading. Near the end of the run note it again. Multiply the difference by 6400 and divide by the elapsed time in minutes and this will be the average speed.

Camera

51. Load the film holder in the dark room by sliding Kodak 2415 35mm film into the holder with the emulsion side up until it hits the end stop. Cut the film off at the end of the holder and place the holder into a plate holder, close the cover.

52. Switch plate holder drive to OUT, with the slot door open, press the shift button until plate position dial stops turning (dial is on the side of plate holder slot).

53. Switch plate holder drive to IN, place plate holder in slot as far as it will go and push on it gently while you push the plate shift button.

54. As soon as the plate has cleared the door, close the slot door.

55. Set the exposure time. Turn the exposure time dial until the numbers are near the top. Loosen the knurled knob, turn the light outer portion of the dial until the black line is opposite the desired number of SECONDS of exposure. Tighten the knob.

56. Turn the exposure interval to the number of minutes desired between exposures.

57. Turn exposure time dial until camera pilot light comes on and then just a little further until it goes out again. Hold the dial so it doesn't move.
58. Turn on the automatic photo switch and release the dial, the first picture will be taken. If it is desired to go one interval before the first picture, release the dial before switching on the auto photo switch.

    Note: To take pictures at various exposures and intervals, keep the auto photo switch off.
59. To remove the photo plate, turn the plate holder to OUT and press the plate shift button until the indicator stops. THEN OPEN THE SLOT DOOR and continue moving the plate out. This will insure that the film is covered before the door is opened.

Shutdown

60. When the timer reaches zero the rotor will brake to a stop at the rate set, usually RAPID. The diffusion pump will also shut off.
61. Turn the refrigeration off.
62. When the rotor stops, the light on the left of the tach will come on.
63. Wait at least 5 minutes after the diffusion pump shut off to turn off the vacuum pump and slowly open the air valve.
64. Turn off the temperature control.
65. Turn off the Laser and put covers on two Laser Mirrors.
66. Turn off the Diffusion Pump switch (the pump is already off) and close the water valve.
67. Turn the voltage control knob to its extreme counterclockwise position. Put braking switch to SLOW.
68. Check to be sure area below chamber is CLEAR.
69. Open Vacuum Chamber. Place coupling wrench on support forks.
70. Loosen rotor by turning clockwise (view from the top).

71. Remove the wrench and unscrew the coupling, push it up.
72. Put the protective cap on the bottom of the rotor. Remove the rotor from the chamber and place it in its stand.
73. Wipe out the chamber with a dry rag.
74. Check to be sure the top of the chamber is CLEAR, close the chamber and put the hoist switch in SAFE.
75. Make sure the braking rate is on SLOW or damage could result the next time the rotor is started.
76. Shut off main power switch.

Calibration of the Rotor Thermistor

The thermistor located in the base of the rotor is the sensing element for the rotor temperature control. The temperature in the rotor is determined by balancing a resistance bridge. Therefore, the reading of temperature is in resistance and that must be converted to ° C.

The thermistor calibration is performed in two steps; one step for temperatures above ambient and one step for sub-ambient temperatures. For above ambient temperatures, leave the rotor in an oven at 40° C overnight to allow it to come to thermal equilibrium. Prepare a suitable insulated container, usually a box filled with styrofoam beads works best. Remove the rotor from the oven, place it on its calibration stand. Plug the stand into the front of the ultracentrifuge, in the socket marked, Thermistor Calibration. The calibration stand will make a complete circuit with the thermistor and allow a reading of the temperature on the centrifuge bridge circuit. Turn on the temperature circuit in the centrifuge, see steps 21-24 and 27 above. There should be a reading from the rotor now, if not, make sure that the circuit is complete. Once that is done, place a thermometer in the special well, with a little oil to assure thermal contact, and place it in the sample hole of the rotor. Now fully insulate the rotor and take readings of the bridge circuit and temperature as the temperature slowly decreases. If the rotor is properly insulated it will take all day to reach 30° C. Repeat the above procedure for sub-ambient calibration, only store the rotor in a refrigerator overnight first.

Once the two calibrations have been completed, the results can be plotted and a straight line drawn through the points, this becomes the calibration, see figure A-1.

APPENDIX B

LASER LIGHT SOURCE FOR MODEL E ULTRACENTRIFUGE INSTALLATION AND ALIGNMENT

A mercury arc lamp was originally used with the Beckman Model E Ultracentrifuge's Rayleigh interference optical system. However, this light source will not allow detection of fringes in the low molecular weight systems being studied here. The solution was to add a laser light source. The installation presented here is modeled after a system built by Dr. R. C. Williams at Vanderbilt University (Williams, 1972; 1978; 1985). A detailed description of the installation is given here. Alignment of the laser optics is similar to that used for the mercury arc optics, but there are enough differences that a description of this important procedure is warranted.

Laser Installation on a Model E Ultracentrifuge

To better understanding the general layout of the optical system please refer to Figure 3-5.

1. A 5 milliwatt HeNe laser (Spectra Physics Model 105) was mounted vertically on the left side the chamber pointing downward (using a Newport, Fountain Valley, CA, Model 806 laser mount on a Newport Model URL-18 optical track). The optical track was centered on the side of the centrifuge according to the location of the existing 45° mirror above the chamber (that mirror defines the optical path through the machine). The distance from the back of the machine to this existing mirror was measured and used as a reference in mounting the laser.
2. The optical track (Newport model URL-36) inside of the barricade was then cut to

size, located and mounted. Two brackets were made of 1" aluminum angle with slots allowing for vertical motion of the bracket and front to back motion of the track. The track was located as low as possible, without interfering with the hoist operation; there is at least a 1/4 to 3/8 inch clearance between the chain and the track over its entire motion. The track was then centered about the location of the laser, i.e., the center of the track must be the same as that of the laser, and leveled. It was leveled very well in two directions (a round bubble level worked best), and bolted down. The leveling could be different in the bolted position so it was checked again. A spatial filter (Newport Model 900 with a 25μm pinhole and 10x objective lens) was then mounted on the track with a stage (Newport Model TSX-1A, stage and B-1A adapter) allowing left to right fine adjustment. The distance measured from the bottom of the barricade to the center of the filter along with the center line of the laser (the optical path through the chamber) locates the hole through the barricade. A large, 1-inch hole, was then drilled in the barricade. When drilling, care was taken not to get metal filings in the drive chain.

3. The 45° mirror outside the chamber (directly below the laser) was then located. Its track (a piece of track left from that used inside the barricade was used) was mounted parallel with the bottom of the machine and centered about the hole in the chamber. The mirror (Newport, round Pyrex (.75" dia. x .18" thick) with substrate 07D20 and coating BD.1, supported in a Newport turret mount, TM-75 with a cover, TMC) was mounted on a 90° bracket (Newport model 360-90); the bracket is adjustable front to back on the track. The mirror was mounted on an adjustable stage (Newport model TSX-1A) which allows fine vertical motion of the mirror on the bracket. The mirror and mount can be moved in a coarse fashion in

and out from the machine on the bracket. Using that coarse adjustment the mirror is aligned with the laser beam, and locked in place. Fine adjustments on the angle of the beam are made later. Fine adjustments on the vertical location can be made with the movable mount.

4. To begin aligning the various components, the collimating lens was removed. A thread with a small weight (a cotter pin is sufficient) was put through the center of a round piece of index card the size of the collimating lens and placed in the collimating lens mount.
5. The first mirror below the laser was adjusted such that the beam hit the thread hanging from the collimating lens mount. The height of this beam, adjusted with the outside mirror mount, must match the spatial filter (which is attached to a mount which will allow about a 1" movement in the direction of the track). This was accomplished by removing the objective lens and pinhole from the spatial filter and replacing the objective lens with a small cardboard mask with a 1 mm hole in the center. That mask was made with a compass, using its point for the hole. The height and direction of the first mirror was adjusted until the beam passed through the mask's hole to hit the thread. The spatial filter was moved as far as possible and checked to be sure that the beam still passed through the hole. Then the spatial filter and mount were moved to the other side of the thread and checked again to see that the beam still passes through the hole. Finally, the spatial filter was moved back and the objective lens installed. The beam should still hit the thread; if it does not, the angle of the and height of the mirror must be adjusted again.
6. The pinhole and objective lens were then reinstalled in the spatial filter and the objective lens focused with a knife edge test. That is, the location of the objective

lens was adjusted on the spatial filter mount until the image disappeared with just the slightest movement of the pin hole. At this point the beam must still be centered on the thread. If not, step 5 was repeated.

7. As a last verification, the spatial filter was moved along its path to insure that the image was still centered on the target; if not steps 5 and 6 were repeated. The assembly was then moved to the other side of the assembly and this test repeated. If the beam was not nearly centered, steps 5 and 6 were repeated. At this point the beam was centered on the true optical path.
8. The second 45° mirror (Newport, round Pyrex (.75" dia. x .18" thick) with substrate 07D20 and coating BD.1, supported in a Newport turret mount, TM-75 with a cover, TMC) was installed with a stage (Newport model TSX-1A) and specially made spacer (a piece of the optical track was cut and machined to the correct thichness, it was then mounted transversely on the track) on the inside optical track. The height of the spacer was designed such that the beam hit the mirror nearly in the center when the mirror was at a 45° angle. Shims were used under the spacer to add additional height. The mirror was mounted in the center of the track, directly under the collimating lens; the beam should automatically be centered front to back. The mirror was attached to a mount that allows right to left movement.
9. The angle of the mirror was adjusted to 45° by placing a piece of lens paper over the mirror and putting a 45° level on the mirror. The mirror was then locked in place.

Now that all laser optical components were installed, fine optical alignment had to be carried out.

Laser Optical System Alignment

This section describes a procedure for alignment of the laser optics. It is very similar to that used for the conventional light source. However, some differences exist so the entire procedure is given here. The main reference for alignment is Gropper (1964) with ideas taken from other sources listed in Chapter 3 and from Williams (1985).

Before beginning the alignment procedure, the collimating and condensing lenses should be removed and cleaned. The technique found best for cleaning, is to fold several KimWipes into a hard 1/2" strip, to soak one edge of the wipes with acetone, and to wipe their edge once across the lens. The wipes are discarded and the procedure repeated until the lenses are clean. The doublet lense does not need to be taken apart. They should be reassembled in their mounts with the arrows or "V"s pointing out of the chamber and aligned with the white lines on the mounts. The condensing lens mount can only be reinstalled in one way (white line to the right) because of the rotor fork. The collimating lens should be mounted with the white line toward the back of the machine. Also, enough masking tape should be put around their edges to make them snug in the mount to insure that the lenses are immobilized during reinstallation of the mounts.

During cleaning of the lenses gaskets and o-rings should be inspected and replaced if necessary. A coating of Apezion Type L non-silicone vacuum grease should be used if needed.

Adjusting the height of the light source. On the laser based system, this adjustment is actually a horizontal adjustment of the spatial filter. The objective of this step is to locate the source of the light (pinhole in spatial filter) such that it is located in the focal plane of the collimating lens.

Light will form a parallel beam after refraction through the collimating lens only if the light source is in the focal plane of the collimating lens. To accomplish this, a piece of black electrical tape, 3/8" wide, is placed across the collimating lens mount, parallel to the front of the machine, without being on the lens. The 45° mirror from the UV system is then mounted on top of a plastic cylinder approximately 2" in diameter, by 3/4" high. A small, very thin shim, is placed under one end of the mirror whose face should point into the cylinder. The mirror should be lightly typed in place. The plastic cylinder and mirror are placed on top of the collimating lens mount, which is then lightly typed in place with the shim toward the front of the machine.

The chamber is then closed. A check is now made to see if the reflected doublet appears on the 45° mirror directly below the chamber using a white card held above the 45° mirror. The card is moved around to locate the reflected doublet without blocking out the incident beam. Once the reflection is found, check to see that both sides of the doublet are present; if not, adjust the tape in the chamber. If the doublet is not hitting the mirror below the chamber, adjust the mirror in the chamber. If it is not found at all, the shim under the mirror in the chamber is probably too thick. When the doublet is reflected from the chamber onto the 45° mirror below the chamber, evacuate the chamber to seat the collimating lens.

The doublet should now be reflected to the pinhole, where a piece of cardboard is taped as close as possible to the pinhole. Care must be taken not to disturb the pinhole. The image should be just to the side of the pinhole; this is caused by the tilt of the mirror in the chamber. It should be projected onto the cardboard in the same plane as the pinhole.

A doublet is formed when the spatial filter (pinhole) is not in the correct location, as observed with a mounted telescope. One person should observe the image, while a second person adjusts the location of the spatial filter along the optical track. The observer will see the doublet become a singlet when the spatial filter (pinhole) is in the correct position. The doublet will form again when the spatial filter (pinhole) is moved beyond the correct position. Lock the spatial filter in place.

Positioning the light source on the axis of the cell. There is a need to have the light enter the sample cell parallel to the meniscus. This can be insured by testing to see if the light is parallel to the axis of rotation. In the laser-based system, this involves moving the 45° mirror between the spatial filter and the collimating lens.

A standard cell is assembled with a mirror as the lower window. This is loaded, with the appropriate counterbalance, into the rotor and spun at about 7000 rpm. The 45° mirror below the chamber is approximately located by observing the collimating lens with a hand mirror and adjusting the 45° mirror until the light image is over the collimating lens.

Using a small calling card, with a piece of black tape along the backside of one edge (to prevent the transmitted light from interfering with the observation of the reflected light) observe the reflected image. Using the fine right-to-left adjustment on the mount and the rotational adjustments on the mirror support (loosen the side set screw and move with the aid of an Allen wrench) the 45° mirror can be adjusted so that the reflected image is observed moving through the transmitted light. Rotational adjustments to the 45° mirror are equivalent to front-back adjustments to the conventional mercury arc lamp. The 45° mirror is aligned when the reflected image is superimposed over the transmitted beam.

At this point an observation should be made of the location of the transmitted image in relation to the collimating lens. If the beam is not hitting entirely on the collimating lens, but is only partially hitting the mount, the angle of the 45° mirror could be in error. Adjust the angle of the mirror to bring the image back on top of the collimating lens and redo the card test above. The angle is adjusted by slightly loosening the set screw on the side of the mirror mount and turning the Allen screw on the axis of the mirror. By loosening the side set screw the rotation is also loosened and the mirror could move rotationally, disturbing the results of the above card test. If that does not correct the problem, return to the thread test (step 5 of the laser installation) and readjust the laser alignment.

Adjusting the 45° mirror above the chamber and position the camera and cylindrical lenses. Note the current locations of the camera and cylindrical lenses on the optical track and then remove them. These lenses should be cleaned in the same manner as described above for the collimating and condensing lenses. A small metal disk with a 1/8" hole in its center is installed in a special holder in the rotor. The disk used here was a Beckman part made for this purpose, but a cardboard mask with a 1/8" hole in the center can be substituted. The rotor is then mounted on the drive and the chamber closed to within 2" of the top.

Remove the right outer panel from the centrifuge; this will expose the photo plate housing. The back of the photo plate holder has had a hole cut in it and is normally covered with a piece of black cardboard, tightly secured with black tape. Removing that covering and the photo plate holder, the shutter should now be in view. Place a thin piece of cardboard, with a large cross marked on its center (target), over the opening and carefully locate the target in the center of the opening. Now open the shutter; the laser light should be visible as a small dot near the target.

Adjust the rotor slightly to get light as near as possible to the mark. Close the chamber so that the rotor will not be moved. Now adjust the 45° mirror above the chamber until the light image hits the center of the target exactly and lock it in place.

Reinstall the camera lens at its former position. Adjust the camera lens front-to-rear (of the machine) until the light image is centered at about the target's vertical line. Then hold a piece of paper about 1" from the side of the camera lens facing the target. Rotate the lens about its vertical axis to center any reflections off the lens about the normal image. Remove the paper and adjust the vertical height of the lens until the image is centered on the target.

Reinstall the cylindrical lens. Adjust the height of this lens until the image (which is now more like a horizontal slit than a round circle) is centered about the horizontal line on the target. Replace the black cardboard covering with black tape, so that it is light proof.

Focusing the camera lens on the midpoint of the cell. Move the phase plate to 90.5°. Place a special ruled glass disk, face down in the same disk holder used in the previous step. Place it in the rotor so that the lines are perpendicular to the radius of the rotor. To obtain diffuse light, a well-stoppered small plastic flat-sided Falcon Flask, with just enough dilute milk to cover the bottom of the flask, is placed over the collimating lens. (The dilution of the milk and the amount of solution in the flask are determined by trial and error.) Close the chamber and observe the image in the viewer. If the lines from the ruled disk cannot be seen, the milk solution is too dense, if the image sparkles, the milk solution is too weak or thin. The optimal dilution yields a clear image. Make any needed adjustments on the milk solution and close the chamber. Move the camera lens in increments (about 1/8" initially) about its current location, taking photos at each location. When the camera is out of focus, the image show slight twisting of the lines from the ruled glass when examined under magnification on a light table. The twisting will change direction as the focal position is passed. By observing these images at different locations of the camera lens, the proper camera focus can be determined and the camera lens secured.

Focusing the cylindrical lens on the plane of the Schlieren analyzer. Place the Falcon Flask and milk solution in front of the 45° mirror above the chamber (i.e., place the flask over the hole leading to the chamber). Rotate the Schlieren analyzer to 90° and slide the cylindrical lens along the track, taking photos. Choose the location of the cylindrical lens that gives the sharpest focus of the analyzer element. Secure the cylindrical lens and move the analyzer element out of the nondiffuse light beam.

Adjusting the interference mask and final adjustment of the cylindrical lens. With the rotor and Falcon Flask removed, the Rayleigh interference mask is installed in its holder. The mask can be properly adjusted using a special Beckman aligning tool that mounts on the drive and extends a reference bar over the mask. The mask is rotated and moved left-to-right in its holder until the alignment tool is directly between, and parallel to, the two slits in the mask.

As a final adjustment, a photo is taken, with and without the cylindrical lens in place (make sure the location of the cylindrical lens is marked before it is removed) without advancing the film (the exposure time without the cylindrical lens should be about 1/10 of that used with the lens in). This image will show horizontal fringes in the center (from the first exposure) and a heavy line at the top and the bottom (from the second exposure). If the fringes are curved in any way, the interference mask should be readjusted. If the fringes are not centered within the dark lines, the height of the cylindrical lens should be adjusted. Finally, if the fringes are on an angle within the heavier lines, the angle of the cylindrical lens should be adjusted. These adjustments should be repeated until a satisfactory photo is obtained.

APPENDIX C

FORTRAN PROGRAM FOR CONVERSION OF FRINGE MEASUREMENTS TO COMPOSITION PROFILES IN THE ULTRACENTRIFUGE

FRNGCNV AND FRNGCNVP

As described in Chapter 3, a microcomparator is used to measure the distance between shifted fringes on a photo negative from the ultracentrifuge. The fringe readings taken on the microcomparator are relative to two reference marks on the negative. These two reference marks are from reference holes in the counterbalance in the rotor, whose distance from the center of the rotor is known. The average of two fringe measurements is converted by the FORTRAN programs FRNGCNV and FRNGCNVP using the following equation

$$c_i = 5.7 + \frac{(r_i - r_1)\,(7.3 - 5.7)}{r_2 - r_1} \qquad \text{(C-1}$$

where c_i are the actual radial locations of fringe (i) in centimeters, r_i is the microcomparator measurement of the fringe (i) and r_1 and r_2 are the microcomparator measurements of the reference line at the top (center most) and bottom, respectively. The numbers 5.7 and 7.3 are the exact locations of the reference holes from the center of the rotor.

The composition profile is also calculated in both of these programs using the procedure outline in Chapter 3 (see equations 3-9 and 3-10). Refractive index data is needed for that calculation. In either of these programs a correlating equation of the form

$$n = n_A + n_B\, x_1 + n_C\, x_1^2 \qquad \text{(C-2}$$

is used. The programs also have the ability to use various mixing rules for calculating mixture refractive index data from pure component properties only. Further, experimental points of composition and refractive index can be entered with intermediate values interpolated by several methods.

The program FRNGCNVP will calculate the effect of pressure. This is accomplished using the procedure of equations (4-3) through (4-5). For this calculation, the pressure derivative of the refractive index for both the solvent and solute must be specified. The equation used is

$$\frac{dn}{dP} = n_{PA} + n_{PB}\,P \qquad \text{(C-3}$$

where n_{PA} and n_{PB} are given in Table 4-11.

The calculations performed by the FRNGCNV can be duplicated in FRNGCNVP by setting the parameters, n_{PA} and n_{PB}, equal to zero. Therefore, only a listing of FRNGCNVP will be given here. Input files of microcomparator measurememts and of physical properties are required by the program. For a description of the content of these files see the beginning of the program listing. The program also outputs two files. One contains details of the calculations and the other contains only the fringe numbers and radius and composition at each fringe. This second file can be used directly by a Lotus 123 program for the calculation of activity coefficient derivatives (see Appendix F).

Included are a listing of FRNGCNVP with an input files RUN38_1P.DAT and CSAC26P.PRP, these are examples from a carbon disulfide/acetone run. The corresponding output files are RUN38_1P.DTL (details) and RUN38_1P.PRN (composition profile), only the detail file is listed here. Further an example output from FRNGCNV is also given, RUN38_1.DTL

Listing of Computer File CSAC26P.PRP Input to FRNGCNVP

```
pure ri lit data; binary ri, lit data & extrap expt.
volume dippr; ve, data from benson.
ri, regression thru x1 = 0.1611
carbon disulfide
      1.6238 60.61801
acetone
        1.356 73.93067
         3.95   0.3308   0.7936    -0.2353  0 0
    -0.137348 0.183784    1.356
    5.1867e-5 -1.0365e-7
       6.3e-5       0.0
            0     1.356
     0.009465 1.357785
      0.02671 1.360375
      0.02864 1.360988
      0.05624 1.366214
       0.0829    1.3702
       0.0945 1.372275
       0.1611     1.382
```

Listing of Computer File RUN38_1P.DAT Input to FRNGCNVP

```
0.035589      .7958
21379
       0    40.368
       0     5.185
       0    30.471
       0    25.6105
       1    21.5345
       2    17.9545
       3    14.384
       4    10.9227
4.846294     8.267
```

Listing of Computer File RUN38_1.DTL Output from FRNGCNV

```
file:               run38_1.dtl
property file:      csac26.prp
prop file comment:pure ri lit data; binary ri, lit data & extrap expt.
                    volume dippr; ve, data from benson.
                    ri, regression thru x1 = 0.1611
fringe data:        run38_1p.dat

r.i. as a quadratic function of x was used.
a =  -.13735      b =   .18378      c =   1.3560

dn/dp as a linear function of p[atm]., Solvent
ap =   .00000      bp =   .00000
dn/dp as a linear function of p[atm]., Solute
aps =   .00000      bps =   .00000
fringe correction, due to pressure diff >  .000000

initial mole fraction 1:       .35589000E-01

total moles of component 1:    .13084624E-03
calculated moles comp 1:       .13084633E-03
epsilon:                       .10000000E-07
delta n / delta x:             .17400284

fringe number    radius, cm   mole fraction 1 n(eq./data)
solvent surface  6.15008092
  .00000000      6.3711195     .34872844E-01  1.3622420
  1.0000000      6.5564818     .35175625E-01  1.3622948
  2.0000000      6.7192878     .35478551E-01  1.3623475
  3.0000000      6.8816617     .35781623E-01  1.3624002
  4.0000000      7.0390673     .36084839E-01  1.3624530
  4.8462940      7.1598416     .36341562E-01  1.3624976
```

Listing of Computer File FRNGCNVP.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
      implicit real*8(a-h,o-z)
      real*8 n1,n2,n,nn,j,lon,lmbda,nrecal,lmd
      dimension r(100),j(100),c(100),n(100),func(100),w(100),x(100),
     >         dndxf(100),vf(100), psolv(100), psamp(100), frsolv(100),
     >         frsamp(100)
      character*40 propfile, frngfile, file, outfl1, outfl2, name1*10,
     >            name2*10, ans*1, amper*1, comnt(3)*60, date*8, time*8
      character a
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
      common /rdata/ rdata(100),xdata(100)
c
c     propfile: name of property file
c     frngfile: name of fringe property file
c     idata: number of fringes and/or partial fringes
c     w(i): 1/2 width of the cell
c     totmol: total number of moles of component 1 charged
c     rhoave: average density, based on initial volume
c     calmol: calculated number of moles
c     lambda: wavelength of light, m
c     dist: thickness of cell, .012 m
c     xinit: initial molefraction component 1
c     r(1): microcomparator reading of top reference
c     r(2): microcomaprator reading of bottom reference
c     r(i): microcomparator readings of fringe 0 thru j
c     j(1): dummy
c     j(2): dummy
c     j(i): fringe number, starting at 0 corresponding to r(i)
c     c(1): actual known measurement of top reference, cm
c     c(2): actual known measurement of botton reference, cm
c     c(i): distance to fringe in cm
c
c  structure of property file
c  line 1: description of data contained in file
c  line 2: continued description of data
c  line 3: continued description of data
c  line 4: name compound 1
c  line 5: n1, pure volume 1 (cc/gmole)
c  line 6: name compound 2
c  line 7: n2, pure volume 2 (cc/gmole)
c  line 8: v0, v1, v2, v3, v4, v5; ve, excess v parameters, benson x1x2
c  line 9: nc, nb, na, refractive index parameters
```

Listing of Computer File FRNGCNVP.FOR

```
c  line 10: pa, pb, coefficients of the pressure derivative of the r.i.
c  line 11: pa, pb, for solute
c  line 12: xdata(1),rdata(1); comp., refractive index data (optional)
c  line n: continue above
c
c  xdata must include 0.0 and 1.0, pure components and be in assending o
c  xdata must be component 1
c
c  file structure for fringe file
c  line 1: x initial, density
c  line 2: speed
c  line 3: dummy, top reference - microcomparator measurement
c  line 4: dummy, bottom reference - microcomparator measurement
c  line 5: dummy, top of solvent - microcomparator measurement
c  line 6: fringe #, microcomparator measurement
c  line n-5: fringe n - microcomparator measurement
c
11    continue
12    write(*,'('' enter name of fringe data > '',\)')
      read(*,'(a)')frngfile
      write(*,'('' enter name of data data > '',\)')
      read(*,'(a)')propfile
      open (4, file=propfile,status='old',access='sequential')
      open (6, file=frngfile,status='old',access='sequential')
      do 10 i = 1,3
10    read(4,'(a)')comnt(i)
      read(4,'(a)')name1
      read(4,*)n1,v10
      read(4,'(a)')name2
      read(4,*)n2,v20
      read(4,*)v0,v1,v2,v3,v4,v5
      read(4,*)aq,b,cp
      read(4,*)ap,bp
      read(4,*)aps,bps
      irdata = 1
      read(4,*,end=90)(xdata(i),rdata(i),i=1,100)
90    if(rdata(1) .eq. 0.) irdata = 0
c
c  read in fringe data, fringe #, measurement
c  r(1), r(2) are the top and bottom references
c
      read(6,*)xinit,den
      read(6,*)spd
      do 100 i = 1,100
         read(6,*,end=5)j(i),r(i)
100   continue
5     idata = i - 1
```

Listing of Computer File FRNGCNVP.FOR

```
c
c  select the method by which to mix pure refractive indexes
c
101   write(*,110)
110   format(' ',/,' select a r.i. mixing method:',/,
     >             ' mixing rule 1                 - 1',/,
     >             ' mixing rule 2                 - 2',/,
     >             ' mixing rule 3                 - 3')
      if(irdata .eq. 1) write(*,111)
111   format(      ' interpolate r.i. data (r.i.^2) - 4',/,
     >             ' interpolate r.i. data (linear) - 5',/,
     >             ' interpolate r.i. data (ln(ri)) - 6')
      write(*,113)
113   format(      ' enter fixed value for dndx  - 7',/,
     >             ' use mix rule 1 for dndx     - 8',/,
     >             ' use quadratic equation      - 9')
      write(*,112)
112   format(' ',/,' enter selection > ',\)
      read(*,*)imeth
      if((imeth .gt. 3 .and. irdata .eq. 0 .and. imeth .lt. 7) .or.
     >   (imeth .gt. 9) .or. imeth .lt. 1) go to 101
      if(imeth .eq. 7) then
        write(*,114)
114   format(' enter fixed dn/dx > ',\)
        read(*,*)dnxin
      endif
c
c  convert microcomparator readings to actual radius measurements
c  top ref = 5.7 cm
c  bottom ref = 7.3 cm
c
      c(1) = 5.7
      c(2) = 7.3
      delfng = 0.0
      d = 0.012
      lmbda = 6.328e-7
      do 200 i = 3,idata
      c(i) = c(1) + ((r(i) - r(1))*(c(2)-c(1)))/(r(2)-r(1))
      w(i) = 0.01923 * c(i) + 0.01289
c
c  correction due to pressure effect
c
      apsamp = xinit * aps + (1.-xinit) * ap
      bpsamp = xinit * bps + (1.-xinit) * bp
      write(*,*)apsamp,bpsamp
      pause ' '
      if(i .eq. 5) then
```

Listing of Computer File FRNGCNVP.FOR

```
            psolv(5) = pres(c(5),c(3),den,spd)
            frsolv(5) = (ap + bp * ((psolv(5) + 1.)/2.)) * (psolv(5)-1.)
     >               * d/lmbda
            psamp(5) = pres(c(5),c(4),den,spd)
            frsamp(5) = (apsamp + bpsamp * psamp(5))*(psamp(5)-1.)*d/lmbda
            fref = frsolv(5) - frsamp(5)
         endif
         if(i .gt. 5) then
            psolv(i) = pres(c(i),c(3),den,spd)
            psamp(i) = pres(c(i),c(4),den,spd)
            frsolv(i) = (ap + bp*psolv(i)) * (psolv(i) - psolv(i-1))
     >               * d/lmbda + frsolv(i-1)
            frsamp(i) = (apsamp + bpsamp*psamp(i)) * (psamp(i) -
     >                 psamp(i-1)) * d/lmbda + frsamp(i-1)
            delfng = frsolv(i) - frsamp(i) - fref
         endif
200      continue
c
c   calculate effect of pressure
c
         deln = (j(idata) + delfng) * lmbda/d
         lmd = deln / j(idata)
c
c   calculate the total moles charged
c
         totvol = 1.2 * (2.* w(4) + (w(idata)-w(4))) * (c(idata) - c(4))
         rhoave = 1./vol(xinit)
         totmol = totvol * rhoave * xinit
c
c   calculate the x and n profile corresponding to the
c   constraints of the material balance
c
         xg = xinit
         if(n1 .gt. n2) then
c              hin = n1
            hin = n2 + (n1 - n2) * .2
            lon = n2
         else
c              lon = n1
            lon = n2 - (n1 - n2) * .2
            hin = n2
         endif
         xlo = 0.0
         xhi = 1.0
c         n(3) = (n1 + n2) / 2.
         n(3) = (lon + hin) / 2.
c         x(3) = 0.5
```

Listing of Computer File FRNGCNVP.FOR

```
      x(3) = 0.1
      j(3) = 0.0
2000  calmol = 0.0
c
      do 300 i = 4, idata
      n(i) = n(i-1) + (j(i) - j(i-1)) * lmd
1000        v = vol(xg)
            goto (1001,1002,1003,1004,1005,1006,1007,1008,1009),imeth
c  mixing rule 1
1001        x(i) = xmix1(n(i),v,xg)
            go to 1010
c  mixing rule 2
1002        x(i) = xmix2(n(i),v,xg)
            go to 1010
c  mixing rule 3
1003        x(i) = xmix3(n(i),v,xg)
            go to 1010
c  interpolate  data 1/ri
1004        x(i) = xdat4(n(i))
            go to 1010
c  interpolate data linear
1005        x(i) = xdat5(n(i))
            go to 1010
c  interpolate data ln(ri)
1006        x(i) = xdat6(n(i))
           goto 1010
c  fixed dn/dx
1007       delx = (j(i) - j(i-1)) * lmd / dnxin
           x(i) = x(i-1) + delx
           goto 1010
c  dn/dn from mixing rule 1
1008       delx = (j(i) - j(i-1)) * lmd / dndx(i-1)
           x(i) = x(i-1) + delx
           goto 1010
c  n data from quadratic equation
1009       x(i) = xquad(n(i),aq,b,cp)
1010        eps = 1.0d-8
            if(dabs(x(i)-xg) .gt. eps)then
               xg = x(i)
               goto 1000
            endif
c
c  calculate integrand
c
            func(i) = 1.2 * 2. * x(i) * w(i) / v
            if ( i .ge. 5) then
            calmol = calmol + ((func(i) + func(i-1))/2.) * (c(i) - c(i-1))
```

```
         endif
300   continue
      if(calmol .gt. totmol) then
         hin = n(3)
         xhi = x(3)
      else
         lon = n(3)
         xlo = x(3)
      endif
      if(imeth .eq. 7 .or. imeth .eq. 8) then
        if(dabs(xhi-xlo) .lt. eps) goto 3000
      else
        if(dabs(lon-hin) .lt. eps) goto 3000
      endif
      n(3) = (lon + hin)/2.
      x(3) = (xlo + xhi) / 2.
      goto 2000
3000  write(*,'('' enter detailed file name >'',\)')
      read(*,'(a)')outfl1
      write(*,'('' enter profile file name >'',\)')
      read(*,'(a)')outfl2
c
      open (8, file=outfl1,status='new',access='sequential')
      open (7, file=outfl2,status='new',access='sequential')
      avednx = (n(idata) - n(4)) / (x(idata) - x(4))
      write(8,25)outfl1,propfile
25    format(' file:                 ',a40,/,
     >       ' property file:     ',a40)
      write(8,26)comnt(1),comnt(2),comnt(3)
26    format(' prop file comment:',a60,/,19x,a60,/,19x,a60)
      write(8,27) frngfile
27    format(' fringe data:       ',a40)
      if(imeth .eq. 1) write(8,31)
      if(imeth .eq. 2) write(8,32)
      if(imeth .eq. 3) write(8,33)
      if(imeth .eq. 4) write(8,34)
      if(imeth .eq. 5) write(8,35)
      if(imeth .eq. 6) write(8,36)
      if(imeth .eq. 7) write(8,37)
      if(imeth .eq. 8) write(8,38)
      if(imeth .eq. 9) write(8,39)aq,b,cp
      write(8,41)ap,bp,aps,bps,delfng
      write(8,40)xinit,totmol,calmol,eps,avednx
      write(8,45)
      write(8,'('' solvent surface'',f12.8)')c(3)
      write(7,50)(j(i),c(i),x(i),i=4,idata)
      write(8,51)(j(i),c(i),x(i),n(i),i=4,idata)
```

Listing of Computer File FRNGCNVP.FOR

```
31   format(' ',/,' ri interpolated from pure ri using mixing rule 1')
32   format(' ',/,' ri interpolated from pure ri using mixing rule 2')
33   format(' ',/,' ri interpolated from pure ri using mixing rule 3')
34   format(' ',/,' tabulated ri data was used, interpolation (ri^2)')
35   format(' ',/,' tabulated ri data was used, interpolation linear')
36   format(' ',/,' tabulated ri data was used, interpolation ln(ri)')
37   format(' ',/,' fixed value for dn/dx was used')
38   format(' ',/,' dn/dx, calculated from mixing rule 1 was used.')
39   format(' ',/,' r.i. as a quadratic function of x was used.',/,
    >           ' a = ',g12.5,' b = ',g12.5,' c = ',g12.5)
40   format(' ',/,' initial mole fraction 1:     ',g15.8,/,/,
    >           ' total moles of component 1: ',g15.8,/,
    >      ' calculated moles comp 1:     ',g15.8,/,
    >      ' epsilon:                     ',g15.8,/,
    >      ' delta n / delta x:           ',g15.8,/)
41   format(' ',/,' dn/dp as a linear function of p[atm]., Solvent',/,
    >           ' ap = ',g12.5,' bp = ',g12.5,/,
    >           ' dn/dp as a linear function of p[atm]., Solute',/,
    >           ' aps = ',g12.5,' bps = ',g12.5,/,
    >           ' fringe correction, due to pressure diff > ',g12.6)
45   format(' fringe number    radius, cm   mole fraction 1 ',
    >     'n(eq./data)')
50   format(' ',3g20.12)
51   format(' ',4g15.8)
     close(4)
     close(6)
     close(7)
     close(8)
     end

     function vol(x1)
     implicit real*8 (a-h,o-z)
     real*8 n1,n2,nn,n
     common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
     x2 = 1.00 - x1
     vol = x1 * v10 + x2 * v20 + (x1 * x2)*(v0 + v1*(1.0 - 2.0*x1) +
    >   .  v2*(1.0 - 2.0*x1)**2 + v3*(1.0 - 2.0*x1)**3 +
    >      v4*(1.0 - 2.0*x1)**4 + v5*(1.0 - 2.0*x1)**5)
     end

     function dndx(x1)
     implicit real*8 (a-h,o-z)
     real*8 n1,n2,nn,n
     common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
     v = vol(x1)
     x2 = 1.00 - x1
     w = x1*((n1**2-1)/(n1**2+2))*(v10/v) +
```

Listing of Computer File FRNGCNVP.FOR

```
     >     x2*((n2**2-1)/(n2**2+2))*(v20/v)
      dwdx = v10*v20*(((n1**2-1)/(n1**2+2))-((n2**2-1)/(n2**2+2))) /
     >       ((v20 + x1*(v10-v20))**2)
      dndx = 1.5*dsqrt((1-w)/(1+2*w))*dwdx/((1-w)**2)
      end

c
c r.i. mixing rule 1
c
      function xmix1(nin,v,xg)
      implicit real*8 (a-h,o-z)
      real*8 n1,n2,nn,n,nin
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
c
c  ri calculated from mixing rule and pure component ri's
c
      xold = xg
10    xmix1 = (((nin**2-1)/(nin**2+2)) -
     >         ((n2**2-1)*vbar2(xold)/((n2**2+2)*v))) /
     >         (((n1**2-1)*vbar1(xold)/((n1**2+2)*v)) -
     >         ((n2**2-1)*vbar2(xold)/((n2**2+2)*v)))
      if(dabs(xold-xcalc) .gt. 0.00001) then
         xold = xcalc
         goto 10
      endif
      end
c
c r.i. mixing rule 2
c
      function xmix2(nin,v,xg)
      implicit real*8 (a-h,o-z)
      real*8 n1,n2,nn,n,nin
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
c
c  ri calculated from mixing rule and pure component ri's
c
      xold = xg
10    xmix2 = ((nin-1) - (n2-1)*vbar2(xold)/v) /
     >         (((n1-1)*vbar1(xold)/v) -
     >         ((n2-1)*vbar2(xold)/v))
      if(dabs(xold-xcalc) .gt. 0.00001) then
         xold = xcalc
         goto 10
      endif
      end
c
c r.i. mixing rule 3
```

Listing of Computer File FRNGCNVP.FOR

```
c
      function xmix3(nin,v,xg)
      implicit real*8 (a-h,o-z)
      real*8 n1,n2,nn,n,nin
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
c
c  ri calculated from mixing rule and pure component ri's
c
      xold = xg
10    xmix3 = (nin -
     >         (n2*vbar2(xold)/v)) /
     >        ((n1*vbar1(xold)/v) -
     >         (n2*vbar2(xold)/v))
      if(dabs(xold-xcalc) .gt. 0.00001) then
         xold = xcalc
         goto 10
      endif
      end

c
c partial molar volume 1
c
      function vbar1(x)
      implicit real*8 (a-h,o-z)
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
      a = v0 + v1 + v2
      b = -v0 - 3.0*v1 - 5.0*v2
      c = 2.0*v1 + 8.8*v2
      d = -4.0*v2
      vbar1 = v10 + a + 2.0*b*x + (3.0*c-b)*x**2 + (4.0*d-2.0*c)*x**3
     >      - 3.0*d*x**4
      end

c
c partial molar volume 2
c
      function vbar2(x)
      implicit real*8 (a-h,o-z)
      common v10,v20,v0,v1,v2,v3,v4,v5,n1,n2
      a = v0 + v1 + v2
      b = -v0 - 3.0*v1 - 5.0*v2
      c = 2.0*v1 + 8.8*v2
      d = -4.0*v2
      vbar2 = v20 - b*x**2 - 2.0*c*x**3 - 3.0*d*x**4
      end

c
```

Listing of Computer File FRNGCNVP.FOR

```
c  interpolate r.i. data using ri^2 interpolation
c
      function xdat4(nin)
      implicit real*8 (a-h,o-z)
      real*8 nin
      common /rdata/ rdata(100),xdata(100)
c
c  ri interpolated from experimental ri data
c
      do 10 i = 2, 20
         if((nin .le. rdata(i) .and. nin .ge. rdata(i-1)) .or.
     >      (nin .ge. rdata(i) .and. nin .le. rdata(i-1))) go to 20
10    continue
20    xdat4 = xdata(i-1) + (xdata(i) - xdata(i-1)) *
     >      ((nin**2) - (rdata(i-1)**2)) /
     >      ((rdata(i)**2) - (rdata(i-1)**2))
      end

c
c  interpolate r.i. data using linear interpolation
c
      function xdat5(nin)
      implicit real*8 (a-h,o-z)
      real*8 nin
      common /rdata/ rdata(100),xdata(100)
c
c  ri interpolated from experimental ri data
c
      do 10 i = 2, 20
         if((nin .le. rdata(i) .and. nin .ge. rdata(i-1)) .or.
     >      (nin .ge. rdata(i) .and. nin .le. rdata(i-1))) go to 20
10    continue
20    xdat5 = xdata(i-1) + (xdata(i) - xdata(i-1)) *
     >      (nin - rdata(i-1)) /
     >      (rdata(i) - rdata(i-1))
      end
c
c  interpolate r.i. data using ln(ri) interpolation
c
      function xdat6(nin)
      implicit real*8 (a-h,o-z)
      real*8 nin
      common /rdata/ rdata(100),xdata(100)
c
c  ri interpolated from experimental ri data
c
      do 10 i = 2, 20
```

Listing of Computer File FRNGCNVP.FOR

```
            if((nin .le. rdata(i) .and. nin .ge. rdata(i-1)) .or.
     >         (nin .ge. rdata(i) .and. nin .le. rdata(i-1))) go to 20
10      continue
20      xdat6 = xdata(i-1) + (xdata(i) - xdata(i-1)) *
     >         (dlog(nin) - dlog(rdata(i-1))) /
     >         (dlog(rdata(i)) - dlog(rdata(i-1)))
        end
c
c  use a quadratic in mole fraction to fit data
c
        function xquad(ri,a,b,c)
        implicit real*8(a-h,o-z)
        if(a .ne. 0.0) then
           root = b**2 - 4.*a*(c-ri)
           if(root .le. 0.0) then
              write(*,*)ri,a,b,c,root
              pause ' '
           else
              xquad = (- b + dsqrt(root)) / (2.*a)
c             write(*,*)xquad,ri
           endif
        else
           xquad = (ri - c) / b
        endif
        end
c
c  calculation of pressure in cell as a funtion of location and speed
c
        function pres(rbot,rtop,den,spd)
        implicit real*8(a-h,o-z)
c
c  a, b parameters to r.i. pressure relationship
c  den, average liquid density, g/cc at initial concentration
c  spd, speed in rpm
c
        pres = ((den*1000.)*(spd*3.1415926*2./60.)**2*((rbot/100.)**2/2.
     >         - (rtop/100.)**2/2.) + 100000.) / 101325.
        end
```

APPENDIX D

EXCESS VOLUME AND PARTIAL MOLAR VOLUME CALCULATIONS

The calculation of mixture volume, V, and partial molar volumes, $\overline{V}_i$, are required in the calculation of activity coefficient derivatives from the composition profile obtained in the ultracentrifuge experiment, see equations (3-7) and (3-11). Calculation of binary DCFIs also require these quantities, see equations (5-6) through (5-8). In this study, the Handa and Benson (1979) equation for the excess volume was used.

$$v^E = x_1 (1 - x_1) [\nu_0 + \nu_1 (1 - 2x_1) + \nu_2 (1 - 2x_1)^2 + \nu_3 (1 - 2x_1)^3 + \nu_4 (1 - 2x_1)^4] \qquad \text{(D-1}$$

where the various ν_i are mixture parameters. Using this equation and pure component volumes, the mixture volume and partial molar volumes can be calculated with the following expressions

$$V = x_1 V_1^o + x_2 V_2^o + v^E \qquad \text{(D-2}$$

$$\begin{aligned}\overline{V}_1 = V_1^o &+ (1 - 2x_1 + x_1^2) [\nu_0 + \nu_1 - 2x_1\nu_1 + \nu_2(1 - 2x_1)^2 + \nu_3(1 - 2x_1)^3 \\ &+ \nu_4(1 - 2x_1)^4] + x_1(1 - x_1) [2x_1\nu_1 - 6\nu_3(1 - x_1) (1 - 2x_1)^2 - 8\nu_4(1 - x_1) (1 - 2x_1)^3 \\ &- 2\nu_1 - 4\nu_2 (1 - 2x_1) (1 - x_1)] \qquad \text{(D-3}\end{aligned}$$

$$\begin{aligned}\overline{V}_2 = V_2^o &+ (1 - 2x_2 + x_2^2) [\nu_0 - \nu_1 + 2x_2\nu_1 + \nu_2(2x_2 - 1)^2 + \nu_3(2x_1 - 1)^3 \\ &+ \nu_4(2x_2 - 1)^4] + x_2(1 - x_2) [-2x_2\nu_1 + 6\nu_3(1 - x_2) (2x_2 - 1)^2 + 8\nu_4(1 - x_2) (2x_2 - 1)^3 \\ &+ 2\nu_1 + 4\nu_2 (1 - 2x_2) (x_2 - 1)] \qquad \text{(D-4}\end{aligned}$$

For the centrifuge calculations only three parameters were used in equation (D-1). If more parameters were given in the literature, or if data were reported in a different equation form, the data were refit by simple least squares to the three parameter form. For DCFI calculations, all parameters were used though if data were reported in the literature as a different equation, the data were refit to the five-parameter equation above.

APPENDIX E

CALCULATION OF INITIAL ULTRACENTRIFUGE SPEED

The best results are obtained from the ultracentrifuge when the resulting number of shifted fringes are in the range of 10 to 20. The number of fringes shifted in an experiment is a function of the physical properties, but more importantly it is a function of the initial concentration and speed of rotation. The physical properties are known ahead of time and an estimate of the activity coefficient derivative can be made. To calculate the proper speed, knowing the initial concentration, involves the solution of several simultaneous equations. These are complicated equations, so the equation solving software package TK! Solver was used. The following equations were set up in that system and solved for the rotating speed.

Equation (3-8) is used.

$$j = \frac{d}{\lambda} \frac{dn}{dx_1} \; (x_b - x_t) \qquad \text{(E-1}$$

where x_b and x_t are x_1 at the bottom and top of the cell, respectively. Assuming the initial concentration will equal the average of the concentration at the top and bottom of the cell gives,

$$x_1^o = \frac{x_b + x_t}{2} \qquad \text{(E-2}$$

Knowing the pure component volumes and molecular weights, the average ideal mixture density can be calculated,

$$\rho^{1D} = \frac{M\ x_1^o + M_2\ (1 - x_1^o)}{V_1^o\ x_1^o + V_2^o\ (1 - x_1^o)} \qquad \text{(E-3}$$

assuming that $\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$ and all the other properties are constant over the small concentration difference in the cell, equation (3-7) can be integrated

$$\frac{(M_1 - V_1^o \rho^{1D})\ \omega^2\ (r_b^2 - r_t^2)}{2RT} \simeq \ln \frac{x_b}{x_t} + (x_b - x_t) \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) \qquad \text{(E-4}$$

where r_b and r_t are the radius from the center of the rotor to the bottom and top of the sample solution. Finally, knowing the pure component refractive indexes and using a volume fraction mixing rule the change in refractive index with respect to composition can be calculated,

$$n \simeq \frac{x_1^o\ V_1^o\ n_1}{x_1^o\ V_1^o + (1 - x_1^o)\ V_2^o} + \frac{(1 - x_1^o)\ V_2^o\ n_2}{x_1^o\ V_1^o + (1 - x_1^o)\ V_2^o} \qquad \text{(E-5}$$

or

$$\frac{dn}{dx_1} \simeq \frac{x_1^o\ V_1^o\ V_2^o\ n_2 - x_1^o\ V_2^o\ n_2 + (V_1^o - V_2^o)\ (V_1^o\ n_1 - x_1^o\ V_1^o\ n_1)}{(V_1^o + x_1^o\ V_2^o - x_1^o\ V_1^o)^2} \qquad \text{(E-6}$$

By specifying the pure component properties, the initial concentration of the solute, an approximate activity coefficient derivative and the desired number of fringes, these equations yield the appropriate speed and approximate concentrations at the top and bottom of the cell.

APPENDIX F

RESULTS OF EXPERIMENTAL ULTRACENTRIFUGE MEASUREMENTS ON FIVE BINARY SYSTEMS

Raw data from the ultracentrifuge experiments are contained in a photographic negative of fringes. From that negative, the distance between each fringe can be measured using a microcomparator. To compensate for any misalignment of the microcomparator, two measurements were made on each negative. First, measurements were made with the solution fringes sloping down toward the bottom and then, with the negative turned over (i.e., with the fringes sloping upward toward the bottom). These two sets of measurements were then averaged. Two reference lines of known distance from the center of the rotor appear on each negative from reference holes in the counter weight (in the rotor). These references are used to calculate the actual radial distance of each fringe from the center of the rotor. Then, using the procedure outlined in Chapter 3 with mixture volume and refractive index data, the composition profile is determined as described in Appendix C. From the composition profile, the density and partial molar volume are calculated for each fringe, and then the activity coefficient derivative is determined using equation (3-11). The required physical properties for each of the five systems studied (carbon disulfide in acetone, chloroform in acetone, carbon tetrachloride in acetone, benzene in acetonitrile and carbon tetrachloride in methanol) and the detailed results of each experimental run are given here. The experimental results are listed in order of increasing concentration.

Carbon Disulfide / Acetone System

The volume and refractive index properties given in Table F-1 are required to calculate activity coefficnet derivatives from ultracentrifuge measurements. The excess volume parameters are to be used with equation (D-1), and the refractive index parameters are for use in equation (C-2).

Table F-1
Physical Properties Used With
Carbon Disulfide(1) / Acetone(2) Experiments

	Pure Volumes		Excess Volume			Refractive Index		
T °C	V_1^o cc/gmol	V_2^o cc/gmol	ν_0 cc/gmol	ν_1	ν_2	n_A	n_B	n_C
10.0	59.6189	72.3434	3.574	0.1857	0.3432	1.36405	0.1807	0.0151
25.0	60.6180	73.9307	3.950	0.2524	0.7936	1.35600	0.1838	-0.1373
26.5	60.7212	74.0957	3.950	0.2524	0.7936	1.35554	0.1799	-0.0834
30.0	60.9643	74.4854	4.065	0.2636	0.8956	1.35395	0.1699	0.0517
33.0	61.1754	74.8242	4.065	0.2636	0.8956	1.35243	0.1650	0.0854

Sources: v^E: 10° Extrapolated from Handa and Benson (1979) parameters.
25° and 26.5° uses a refit of four Handa and Benson (1979) parameters at 25°.
30° and 33° uses Handa and Benson (1979) 30° parameters directly.
V^o: Daubert and Danner (1985).
n: Pure data was interpolated from Loiseleur et al. (1967) and Campbell and Kartzmark (1977). Mixture data is reported in Table 4-2.

The following tables detail the measurements made on the carbon disulfide / acetone system.

Table F-2

Run 27-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 42044 RPM
T: 25° C
x_1^o : 0.01051

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.327	0.0098	65.446	0.7889	101.680		
1	6.531	0.0101	65.441	0.7890	98.755	-14.156	84.599
2	6.700	0.0104	65.436	0.7891	95.993	-23.318	72.675
3	6.871	0.0107	65.432	0.7892	93.380	-18.200	75.179
4	7.031	0.0110	65.427	0.7893	90.904	-18.709	72.195
4.80	7.149	0.0112	65.423	0.7894	89.015	-20.509	68.505
				Average		-18.979	74.631
				Std. Dev.		3.004	5.421

Table F-3

Run 39-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 35583 RPM
T: 26.5° C
x_1^o : 0.01876

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.343	0.0178	65.418	0.7898	56.280		
1	6.478	0.0181	65.413	0.7899	55.362	-15.745	39.617
2	6.598	0.0184	65.408	0.7900	54.472	-18.564	35.909
3	6.725	0.0187	65.404	0.7901	53.610	-14.664	38.947
4	6.843	0.0189	65.399	0.7902	52.775	-16.372	36.403
5	6.952	0.0192	65.394	0.7903	51.965	-17.469	34.496
6	7.058	0.0195	65.389	0.7904	51.179	-17.094	34.085
6.969	7.155	0.0198	65.384	0.7905	50.440	-17.822	32.618
				Average		-16.818	36.011
				Std. Dev.		1.227	2.370

Table F-4
Run 39-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 42031 RPM
T: 26.5° C
x_1^o : 0.01876

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.310	0.0173	65.426	0.7896	57.841		
1	6.402	0.0176	65.421	0.7897	56.872	-19.366	37.506
2	6.489	0.0179	65.416	0.7898	55.934	-19.930	36.004
3	6.576	0.0182	65.411	0.7899	55.026	-18.784	36.242
4	6.664	0.0185	65.407	0.7900	54.147	-16.836	37.312
5	6.746	0.0188	65.402	0.7901	53.296	-17.860	35.436
6	6.831	0.0191	65.397	0.7902	52.470	-15.508	36.962
7	6.913	0.0194	65.392	0.7903	51.669	-15.917	35.752
8	6.981	0.0196	65.387	0.7904	50.892	-20.568	30.324
9	7.062	0.0199	65.383	0.7905	50.138	-13.645	36.493
10.188	7.150	0.0203	65.377	0.7906	49.269	-15.891	33.378
				Average		-17.430	35.541
				Std. Dev.		2.119	2.063

Table F-5
Run 24-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 35608 RPM
T: 10° C
x_1^o : 0.02074

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.266	0.0195	63.499	0.8096	51.206		
1	6.381	0.0198	63.496	0.8097	50.455	-14.204	36.251
2	6.502	0.0201	63.493	0.8098	49.725	-11.200	38.525
3	6.622	0.0204	63.489	0.8099	49.016	-9.599	39.417
4	6.735	0.0207	63.486	0.8100	48.327	-10.869	37.459
5	6.839	0.0210	63.483	0.8101	47.657	-12.500	35.157
6	6.942	0.0213	63.480	0.8102	47.006	-11.865	35.141
7	7.035	0.0216	63.476	0.8103	46.372	-13.983	32.389
8	7.127	0.0219	63.473	0.8104	45.755	-13.219	32.537
8.334	7.158	0.0220	63.472	0.8105	45.553	-12.591	32.962
				Average		-12.225	35.537
				Std. Dev.		1.419	2.450

Table F-6
Run 23-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 35605 RPM
T: 25° C
x_1^o : 0.02074

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.250	0.0196	65.285	0.7922	51.089		
1	6.383	0.0199	65.281	0.7923	50.329	-11.669	38.661
2	6.509	0.0202	65.276	0.7924	49.591	-12.333	37.258
3	6.636	0.0205	65.271	0.7925	48.874	-10.787	38.087
4	6.753	0.0208	65.266	0.7926	48.177	-12.330	35.847
5	6.864	0.0211	65.261	0.7927	47.499	-12.680	34.819
6	6.969	0.0213	65.257	0.7928	46.840	-13.613	33.227
7	7.065	0.0216	65.252	0.7929	46.198	-15.213	30.985
8	7.155	0.0219	65.247	0.7930	45.574	-16.440	29.133
8.034	7.158	0.0220	65.247	0.7930	45.553	-16.058	29.495
				Average		-13.458	34.168
				Std. Dev.		1.893	3.440

Table F-7
Run 23-3 Carbon Disulfide(1) / Acetone(2)
Average Speed: 25980 RPM
T: 25° C
x_1^o : 0.02074

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.248	0.0202	65.276	0.7924	49.567		
1	6.540	0.0205	65.271	0.7925	48.850	-3.965	44.885
2	6.797	0.0208	65.266	0.7926	48.154	-6.713	41.441
3	7.002	0.0211	65.261	0.7927	47.477	-13.289	34.188
3.770	7.159	0.0213	65.258	0.7927	46.968	-11.769	35.199
				Average		-8.934	38.928
				Std. Dev.		3.763	4.421

Table F-8
Run 25-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 35599 RPM
T: 30° C
x_1^o : 0.02074

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.242	0.0195	65.837	0.7862	51.306		
1	6.357	0.0198	65.831	0.7863	50.511	-19.185	31.326
2	6.488	0.0201	65.826	0.7864	49.741	-13.375	36.365
3	6.612	0.0204	65.821	0.7865	48.994	-13.667	35.327
4	6.735	0.0207	65.815	0.7866	48.269	-12.647	35.621
5	6.843	0.0210	65.810	0.7867	47.565	-15.637	31.927
6	6.949	0.0213	65.805	0.7868	46.881	-15.101	31.780
7	7.050	0.0216	65.799	0.7869	46.217	-15.468	30.750
8	7.146	0.0219	65.794	0.7870	45.572	-15.903	29.669
8.114	7.157	0.0220	65.794	0.7870	45.500	-15.424	30.076
				Average		-15.156	32.538
				Std. Dev.		1.791	2.400

Table F-9
Run 37-3 Carbon Disulfide(1) / Acetone(2)
Average Speed: 29499 RPM
T: 18.8° C
x_1^o : 0.02846

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.222	0.0274	64.543	0.8007	36.449		
1	6.366	0.0277	64.539	0.8008	36.055	-7.238	28.817
2	6.511	0.0280	64.535	0.8009	35.670	-6.108	29.562
3	6.653	0.0283	64.531	0.8010	35.293	-5.602	29.691
4	6.787	0.0286	64.527	0.8011	34.924	-6.385	28.539
5	6.912	0.0289	64.522	0.8012	34.562	-7.372	27.190
6	7.037	0.0292	64.518	0.8014	34.207	-6.572	27.636
7	7.146	0.0295	64.514	0.8015	33.860	-9.154	24.706
7.097	7.157	0.0296	64.513	0.8015	33.826	-8.743	25.083
				Average		-7.147	27.653
				Std. Dev.		1.173	1.783

Table F-10
Run 37-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 21719 RPM
T: 26.5° C
x_1^o : 0.02846

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.232	0.0279	65.255	0.7932	35.822		
1	6.490	0.0282	65.250	0.7933	35.442	-8.244	27.198
2	6.761	0.0285	65.246	0.7934	35.069	-5.340	29.729
3	6.996	0.0288	65.241	0.7935	34.705	-7.885	26.819
3.694	7.160	0.0290	65.238	0.7936	34.456	-6.718	27.738
				Average		-7.047	27.871
				Std. Dev.		1.135	1.121

Table F-11
Run 38-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 21739 RPM
T: 26.5° C
x_1^o : 0.03558

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.371	0.0349	65.147	0.7956	28.676		
1	6.556	0.0352	65.142	0.7957	28.429	-8.714	19.714
2	6.719	0.0355	65.137	0.7958	28.186	-10.378	17.809
3	6.882	0.0358	65.133	0.7959	27.947	-9.756	18.191
4	7.039	0.0361	65.128	0.7960	27.712	-9.663	18.050
4.846	7.160	0.0363	65.124	0.7961	27.517	-10.787	16.730
				Average		-9.859	18.099
				Std. Dev.		0.706	0.957

Table F-12
Run 38-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 29502 RPM
T: 26.5° C
x_1^o : 0.03558

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.357	0.0343	65.156	0.7954	29.195		
1	6.452	0.0346	65.151	0.7955	28.939	-10.301	18.638
2	6.549	0.0349	65.147	0.7956	28.688	-9.523	19.164
3	6.640	0.0352	65.142	0.7957	28.441	-10.017	18.424
4	6.731	0.0355	65.137	0.7958	28.198	-9.674	18.524
5	6.823	0.0358	65.133	0.7959	27.959	-8.904	19.055
6	6.914	0.0361	65.128	0.7960	27.724	-8.748	18.976
7	7.000	0.0364	65.124	0.7961	27.493	-9.231	18.262
8	7.083	0.0367	65.119	0.7962	27.265	-9.478	17.787
8.939	7.157	0.0370	65.114	0.7963	27.055	-9.792	17.263
				Average		-9.519	18.455
				Std. Dev.		0.473	0.585

Table F-13
Run 38-3 Carbon Disulfide(1) / Acetone(2)
Average Speed: 37000 RPM
T: 26.5° C
x_1^o : 0.03558

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.359	0.0335	65.168	0.7951	29.853		
1	6.419	0.0338	65.163	0.7952	29.586	-10.865	18.721
2	6.482	0.0341	65.158	0.7953	29.323	-9.882	19.441
3	6.541	0.0344	65.154	0.7954	29.066	-10.418	18.648
4	6.602	0.0347	65.149	0.7955	28.812	-9.632	19.180
5	6.659	0.0350	65.144	0.7956	28.563	-10.293	18.271
6	6.717	0.0353	65.140	0.7957	28.318	-9.744	18.574
7	6.776	0.0356	65.135	0.7958	28.077	-8.950	19.128
8	6.834	0.0359	65.130	0.7960	27.840	-8.889	18.952
9	6.889	0.0362	65.126	0.7961	27.607	-9.174	18.433
10	6.947	0.0365	65.121	0.7962	27.378	-8.185	19.193
11	7.000	0.0368	65.117	0.7963	27.152	-9.494	17.658
12	7.055	0.0371	65.112	0.7964	26.930	-8.223	18.707
13	7.106	0.0374	65.107	0.7965	26.712	-9.372	17.340
14	7.156	0.0377	65.103	0.7966	26.496	-9.542	16.955
14.021	7.157	0.0377	65.102	0.7966	26.492	-9.416	17.076
				Average		-9.472	18.418
				Std. Dev.		0.717	0.773

Table F-14
Run 38-4 Carbon Disulfide(1) / Acetone(2)
Average Speed: 29461 RPM
T: 26.5° C
x_1^o : 0.03558

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.357	0.0343	65.156	0.7954	29.195		
1	6.453	0.0346	65.151	0.7955	28.939	-10.194	18.745
2	6.549	0.0349	65.147	0.7956	28.688	-9.728	18.960
3	6.640	0.0352	65.142	0.7957	28.441	-10.135	18.306
4	6.728	0.0355	65.137	0.7958	28.198	-10.184	18.014
5	6.820	0.0358	65.133	0.7959	27.959	-9.145	18.814
6	6.911	0.0361	65.128	0.7960	27.724	-8.750	18.973
7	7.004	0.0364	65.124	0.7961	27.493	-7.642	19.851
8	7.083	0.0367	65.119	0.7962	27.265	-10.359	16.906
8.877	7.157	0.0369	65.115	0.7963	27.069	-8.849	18.219
				Average		-9.443	18.532
				Std. Dev.		0.861	0.768

Table F-15
Run 26-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 28020 RPM
T: 25° C
x_1^o : 0.03767

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.349	0.0364	65.021	0.7979	27.502		
1	6.459	0.0367	65.016	0.7980	27.274	-7.982	19.292
2	6.557	0.0370	65.011	0.7981	27.050	-9.454	17.596
3	6.651	0.0373	65.007	0.7982	26.830	-9.623	17.207
4	6.745	0.0376	65.002	0.7983	26.613	-9.292	17.321
5	6.831	0.0379	64.997	0.7984	26.399	-10.414	15.985
6	6.919	0.0382	64.993	0.7985	26.189	-9.650	16.538
7	7.000	0.0385	64.988	0.7986	25.982	-10.428	15.553
8	7.078	0.0388	64.983	0.7987	25.778	-10.759	15.018
9	7.153	0.0391	64.979	0.7988	25.577	-10.816	14.760
9.023	7.155	0.0391	64.979	0.7988	25.572	-10.658	14.914
				Average		-9.908	16.419
				Std. Dev.		0.842	1.379

Table F-16
Run 26-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 21707 RPM
T: 25° C
x_1^o : 0.03767

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.349	0.0370	65.011	0.7981	27.021		
1	6.561	0.0373	65.006	0.7982	26.801	-4.482	22.319
2	6.751	0.0376	65.001	0.7983	26.585	-5.816	20.768
3	6.921	0.0379	64.997	0.7984	26.371	-7.283	19.088
4	7.064	0.0382	64.992	0.7985	26.162	-9.797	16.364
4.727	7.157	0.0384	64.989	0.7986	26.011	-10.998	15.013
				Average		-7.675	18.711
				Std. Dev.		2.423	2.705

Table F-17
Run 53-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 25968 RPM
T: 26.5° C
x_1^o : 0.05806

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.225	0.0560	64.832	0.8029	17.850		
1	6.301	0.0563	64.828	0.8030	17.751	-6.889	10.862
2	6.379	0.0566	64.823	0.8031	17.653	-6.513	11.140
3	6.452	0.0570	64.819	0.8032	17.556	-6.830	10.726
4	6.530	0.0573	64.814	0.8033	17.460	-6.054	11.406
5	6.602	0.0576	64.810	0.8034	17.364	-6.659	10.705
6	6.672	0.0579	64.806	0.8035	17.270	-6.749	10.521
7	6.743	0.0582	64.801	0.8036	17.177	-6.445	10.732
8	6.815	0.0585	64.797	0.8037	17.085	-6.088	10.997
9	6.882	0.0588	64.792	0.8038	16.993	-6.572	10.421
10	6.950	0.0592	64.788	0.8040	16.903	-6.346	10.557
11	7.015	0.0595	64.783	0.8041	16.814	-6.555	10.258
12	7.079	0.0598	64.779	0.8042	16.725	-6.559	10.166
13	7.139	0.0601	64.774	0.8043	16.637	-7.047	9.590
13.331	7.159	0.0602	64.773	0.8043	16.608	-6.941	9.668
				Average		-6.589	10.553
				Std. Dev.		0.285	0.494

Table F-18
Run 53-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 29503 RPM
T: 26.5° C
x_1^o : 0.05806

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.225	0.0554	64.841	0.8027	18.047		
1	6.288	0.0557	64.837	0.8028	17.946	-6.425	11.521
2	6.348	0.0560	64.832	0.8029	17.846	-6.758	11.087
3	6.405	0.0563	64.828	0.8030	17.747	-7.045	10.701
4	6.461	0.0567	64.823	0.8031	17.648	-7.085	10.564
5	6.521	0.0570	64.819	0.8032	17.551	-6.115	11.436
6	6.577	0.0573	64.814	0.8033	17.455	-6.876	10.579
7	6.631	0.0576	64.810	0.8034	17.360	-6.904	10.456
8	6.686	0.0579	64.805	0.8035	17.266	-6.505	10.761
9	6.738	0.0582	64.801	0.8036	17.173	-6.931	10.242
10	6.792	0.0585	64.796	0.8037	17.081	-6.407	10.674
11	6.844	0.0589	64.792	0.8039	16.989	-6.716	10.274
12	6.897	0.0592	64.787	0.8040	16.899	-6.348	10.551
13	6.949	0.0595	64.783	0.8041	16.809	-6.315	10.495
14	6.998	0.0598	64.779	0.8042	16.721	-6.643	10.078
15	7.048	0.0601	64.774	0.8043	16.633	-6.403	10.231
16	7.094	0.0604	64.770	0.8044	16.547	-7.111	9.435
17	7.139	0.0608	64.765	0.8045	16.461	-7.160	9.301
17.433	7.158	0.0609	64.763	0.8046	16.424	-7.068	9.356
				Average		-6.712	10.430
				Std. Dev.		0.318	0.605

Table F-19
Run 30-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 17968 RPM
T: 10° C
x_1^o : 0.10949

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.403	0.1079	62.623	0.8413	9.270		
1	6.474	0.1082	62.620	0.8414	9.245	-3.644	5.601
2	6.544	0.1085	62.618	0.8415	9.221	-3.632	5.589
3	6.614	0.1087	62.615	0.8416	9.197	-3.599	5.597
4	6.682	0.1090	62.613	0.8417	9.172	-3.628	5.544
5	6.750	0.1093	62.610	0.8418	9.148	-3.565	5.583
6	6.816	0.1096	62.608	0.8420	9.124	-3.619	5.506
7	6.888	0.1099	62.605	0.8421	9.101	-3.131	5.969
8	6.945	0.1102	62.603	0.8422	9.077	-4.175	4.902
9	7.008	0.1105	62.600	0.8423	9.053	-3.714	5.340
10	7.070	0.1107	62.598	0.8424	9.030	-3.685	5.345
11	7.134	0.1110	62.595	0.8425	9.007	-3.425	5.582
11.417	7.161	0.1111	62.594	0.8425	8.997	-3.365	5.632
				Average		-3.598	5.516
				Std. Dev.		0.235	0.239

Table F-20

Run 29-1 Carbon Disulfide(1) / Acetone(2)
Average Speed: 17978 RPM
T: 25° C
x_1^o : 0.10949

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.418	0.1076	64.054	0.8229	9.293		
1	6.491	0.1080	64.050	0.8230	9.263	-4.702	4.561
2	6.562	0.1083	64.046	0.8231	9.234	-4.704	4.530
3	6.632	0.1086	64.042	0.8232	9.205	-4.681	4.523
4	6.701	0.1090	64.038	0.8234	9.176	-4.753	4.422
5	6.770	0.1093	64.033	0.8235	9.147	-4.610	4.537
6	6.838	0.1097	64.029	0.8236	9.118	-4.663	4.455
7	6.904	0.1100	64.025	0.8237	9.090	-4.653	4.437
8	6.969	0.1104	64.021	0.8239	9.062	-4.703	4.358
9	7.031	0.1107	64.017	0.8240	9.034	-4.837	4.197
10	7.093	0.1110	64.013	0.8241	9.006	-4.740	4.266
11	7.154	0.1114	64.009	0.8242	8.978	-4.795	4.183
11.195	7.166	0.1115	64.008	0.8242	8.972	-4.755	4.217
				Average		-4.716	4.391
				Std. Dev.		0.061	0.136

Table F-21
Run 29-3 Carbon Disulfide(1) / Acetone(2)
Average Speed: 23141 RPM
T: 25° C
x_1^o : 0.10949

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.360	0.1064	64.068	0.8224	9.398		
1	6.409	0.1067	64.064	0.8226	9.368	-4.361	5.006
2	6.454	0.1071	64.060	0.8227	9.338	-4.613	4.725
3	6.502	0.1074	64.056	0.8228	9.308	-4.315	4.993
4	6.548	0.1078	64.052	0.8229	9.279	-4.370	4.908
5	6.592	0.1081	64.048	0.8230	9.249	-4.627	4.622
6	6.638	0.1085	64.044	0.8232	9.220	-4.267	4.953
7	6.682	0.1088	64.040	0.8233	9.191	-4.469	4.722
8	6.727	0.1091	64.036	0.8234	9.162	-4.301	4.861
9	6.770	0.1095	64.032	0.8235	9.133	-4.487	4.647
10	6.813	0.1098	64.027	0.8237	9.105	-4.365	4.740
11	6.857	0.1102	64.023	0.8238	9.077	-4.271	4.805
12	6.901	0.1105	64.019	0.8239	9.048	-4.228	4.820
13	6.942	0.1109	64.015	0.8240	9.020	-4.369	4.651
14	6.983	0.1112	64.011	0.8242	8.992	-4.463	4.529
15	7.024	0.1115	64.007	0.8243	8.965	-4.390	4.574
16	7.064	0.1119	64.003	0.8244	8.937	-4.410	4.527
17	7.104	0.1122	63.999	0.8245	8.910	-4.393	4.517
18	7.141	0.1126	63.995	0.8247	8.882	-4.632	4.251
18.403	7.156	0.1127	63.993	0.8247	8.871	-4.601	4.271
				Average		-4.417	4.691
				Std. Dev.		0.123	0.211

Table F-22
Run 31-2 Carbon Disulfide(1) / Acetone(2)
Average Speed: 17977 RPM
T: 33° C
x_1^o : 0.10949

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.382	0.1080	64.726	0.8132	9.261		
1	6.458	0.1083	64.722	0.8133	9.237	-3.674	5.563
2	6.534	0.1086	64.719	0.8134	9.212	-3.677	5.535
3	6.614	0.1088	64.715	0.8135	9.188	-3.217	5.970
4	6.688	0.1091	64.711	0.8136	9.164	-3.586	5.577
5	6.767	0.1094	64.708	0.8138	9.140	-3.155	5.984
6	6.840	0.1097	64.704	0.8139	9.116	-3.508	5.607
7	6.912	0.1100	64.700	0.8140	9.092	-3.443	5.648
8	6.983	0.1103	64.697	0.8141	9.068	-3.501	5.567
9	7.052	0.1106	64.693	0.8142	9.045	-3.558	5.486
10	7.119	0.1108	64.690	0.8143	9.021	-3.643	5.378
10.692	7.167	0.1110	64.687	0.8143	9.005	-3.414	5.591
				Average		-3.489	5.628
				Std. Dev.		0.165	0.178

Chloroform / Acetone System

The volume and refractive index properties given in Table F-23 are required to calculate activity coefficient derivatives from ultracentrifuge measurements.

Table F-23
Physical Properties Used With
Chloroform(1) / Acetone(2) Experiments

	Pure Volumes		Excess Volume			Refractive Index		
T	V_1^o	V_2^o	ν_0	ν_1	ν_2	n_A	n_B	n_C
°C	cc/gmol	cc/gmol	cc/gmol					
26.5	80.8214	74.0957	-0.3779	0.9118	0.0087	1.35554	0.0928	0
37.3	81.9909	75.3087	-0.5655	0.9775	0.0682	1.34999	0.0924	0

Sources: v^E: 26.5° uses 25° parameters directly from Handa and Benson (1979).
37.3° uses 35° parameters directly from Handa and Benson (1979).
V^o: Daubert and Danner (1985).
n: Pure data was interpolated from Loiseleur et al. (1967) and Campbell and Kartzmark (1977). Mixture data is reported in Table 4-4.

The following tables detail the measurements made on the chloroform / acetone system.

Table F-24
Run 51-2 Chloroform(1) / Acetone(2)
Average Speed: 42007 RPM
T: 26.5° C
x_1^o : 0.01888

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.207	0.0155	81.292	0.7955	64.608		
1	6.295	0.0160	81.289	0.7959	62.319	-21.418	40.901
2	6.384	0.0166	81.286	0.7963	60.186	-18.511	41.675
3	6.468	0.0172	81.284	0.7967	58.195	-17.912	40.284
4	6.549	0.0178	81.281	0.7972	56.332	-17.528	38.804
5	6.631	0.0183	81.279	0.7976	54.583	-14.557	40.026
6	6.709	0.0189	81.276	0.7980	52.941	-14.354	38.587
7	6.783	0.0195	81.274	0.7984	51.394	-14.516	36.878
8	6.854	0.0200	81.271	0.7989	49.935	-14.176	35.759
9	6.925	0.0206	81.268	0.7993	48.556	-12.357	36.200
10	6.991	0.0212	81.266	0.7997	47.252	-13.035	34.217
11	7.057	0.0217	81.263	0.8001	46.016	-11.768	34.248
12	7.121	0.0223	81.261	0.8006	44.843	-11.625	33.218
12.509	7.153	0.0226	81.260	0.8008	44.268	-10.763	33.506
				Average		-14.809	37.254
				Std. Dev.		3.039	2.855

Table F-25

Run 51-3 Chloroform(1) / Acetone(2)
Average Speed: 33432 RPM
T: 26.5° C
x_1^o : 0.01888

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.206	0.0167	81.286	0.7964	59.954		
1	6.340	0.0172	81.284	0.7968	57.978	-18.882	39.096
2	6.473	0.0178	81.281	0.7972	56.128	-16.233	39.894
3	6.610	0.0184	81.278	0.7976	54.392	-12.492	41.900
4	6.719	0.0190	81.276	0.7981	52.761	-18.642	34.118
5	6.836	0.0195	81.273	0.7985	51.224	-14.281	36.943
6	6.944	0.0201	81.271	0.7989	49.775	-14.894	34.881
7	7.050	0.0207	81.268	0.7993	48.405	-13.939	34.466
8	7.150	0.0212	81.266	0.7998	47.108	-13.816	33.293
8.045	7.155	0.0213	81.266	0.7998	47.052	-13.286	33.766
				Average		-15.163	36.484
				Std. Dev.		2.158	2.940

Table F-26
Run 50-1 Chloroform(1) / Acetone(2)
Average Speed: 37026 RPM
T: 26.5° C
x_1^o : 0.02515

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.223	0.0221	81.262	0.8004	45.319		
1	6.320	0.0226	81.259	0.8008	44.181	-9.385	34.795
2	6.413	0.0232	81.257	0.8012	43.098	-9.174	33.924
3	6.504	0.0238	81.254	0.8017	42.067	-8.398	33.669
4	6.591	0.0243	81.252	0.8021	41.085	-8.562	32.523
5	6.675	0.0249	81.249	0.8025	40.147	-8.274	31.873
6	6.761	0.0255	81.247	0.8029	39.251	-6.335	32.916
7	6.837	0.0260	81.244	0.8034	38.394	-8.864	29.531
8	6.916	0.0266	81.242	0.8038	37.574	-6.432	31.142
9	6.989	0.0272	81.239	0.8042	36.788	-7.945	28.843
10	7.058	0.0278	81.237	0.8046	36.035	-8.467	27.568
11	7.130	0.0283	81.234	0.8051	35.311	-6.235	29.076
11.298	7.151	0.0285	81.234	0.8052	35.102	-5.735	29.367
				Average		-7.817	31.269
				Std. Dev.		1.221	2.253

Table F-27
Run 50-2 Chloroform(1) / Acetone(2)
Average Speed: 29511 RPM
T: 26.5° C
x_1^o : 0.02515

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.222	0.0232	81.257	0.8012	43.158		
1	6.376	0.0237	81.254	0.8016	42.124	-7.140	34.985
2	6.510	0.0243	81.252	0.8021	41.139	-9.691	31.448
3	6.648	0.0249	81.249	0.8025	40.199	-7.607	32.592
4	6.776	0.0254	81.247	0.8029	39.301	-8.034	31.267
5	6.900	0.0260	81.244	0.8033	38.442	-7.809	30.633
6	7.017	0.0266	81.242	0.8038	37.620	-8.158	29.462
7	7.128	0.0272	81.239	0.8042	36.832	-8.486	28.346
7.218	7.152	0.0273	81.239	0.8043	36.665	-7.875	28.790
				Average		-8.100	30.940
				Std. Dev.		0.706	2.034

Table F-28
Run 49-2 Chloroform(1) / Acetone(2)
Average Speed: 37019 RPM
T: 26.5° C
x_1^o : 0.03713

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.093	0.0318	81.219	0.8077	31.447		
1	6.166	0.0324	81.217	0.8081	30.895	-5.520	25.375
2	6.227	0.0329	81.214	0.8085	30.362	-8.626	21.736
3	6.287	0.0335	81.212	0.8089	29.847	-8.582	21.265
4	6.349	0.0341	81.210	0.8094	29.349	-7.438	21.911
5	6.407	0.0346	81.207	0.8098	28.867	-7.865	21.002
6	6.465	0.0352	81.205	0.8102	28.401	-7.173	21.227
7	6.521	0.0358	81.202	0.8106	27.950	-7.276	20.674
8	6.577	0.0363	81.200	0.8111	27.512	-6.714	20.798
9	6.627	0.0369	81.198	0.8115	27.089	-8.697	18.391
10	6.687	0.0375	81.195	0.8119	26.678	-4.046	22.632
11	6.742	0.0381	81.193	0.8123	26.279	-5.547	20.732
12	6.793	0.0386	81.190	0.8128	25.892	-6.168	19.724
13	6.844	0.0392	81.188	0.8132	25.517	-5.920	19.597
14	6.896	0.0398	81.186	0.8136	25.152	-5.170	19.982
15	6.946	0.0403	81.183	0.8140	24.797	-5.343	19.454
16	6.992	0.0409	81.181	0.8145	24.453	-6.428	18.024
17	7.040	0.0415	81.178	0.8149	24.117	-5.192	18.926
18	7.079	0.0420	81.176	0.8153	23.791	-8.060	15.731
19	7.129	0.0426	81.174	0.8157	23.474	-3.601	19.873
19.549	7.156	0.0429	81.172	0.8160	23.303	-3.297	20.006
				Average		-6.333	20.353
				Std. Dev.		1.600	1.899

Table F-29
Run 49-3 Chloroform(1) / Acetone(2)
Average Speed: 29501 RPM
T: 26.5° C
x_1^o : 0.03713

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.091	0.0337	81.211	0.8091	29.687		
1	6.196	0.0343	81.209	0.8095	29.194	-6.017	23.177
2	6.287	0.0348	81.206	0.8099	28.718	-8.373	20.344
3	6.381	0.0354	81.204	0.8103	28.256	-7.049	21.207
4	6.470	0.0360	81.202	0.8108	27.810	-7.133	20.677
5	6.561	0.0365	81.199	0.8112	27.377	-6.222	21.154
6	6.647	0.0371	81.197	0.8116	26.957	-6.740	20.217
7	6.729	0.0377	81.194	0.8120	26.550	-6.818	19.732
8	6.814	0.0382	81.192	0.8125	26.156	-5.676	20.480
9	6.893	0.0388	81.190	0.8129	25.772	-6.325	19.447
10	6.971	0.0394	81.187	0.8133	25.400	-5.950	19.450
11	7.045	0.0399	81.185	0.8137	25.039	-6.615	18.424
12	7.116	0.0405	81.182	0.8142	24.687	-6.595	18.092
12.563	7.157	0.0408	81.181	0.8144	24.494	-6.224	18.269
				Average		-6.595	20.052
				Std. Dev.		0.661	1.345

Table F-30
Run 49-4 Chloroform(1) / Acetone(2)
Average Speed: 25969 RPM
T: 26.5° C
x_1^o : 0.03713

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.089	0.0345	81.208	0.8097	29.016		
1	6.219	0.0350	81.206	0.8101	28.545	-6.439	22.106
2	6.337	0.0356	81.203	0.8105	28.090	-7.481	20.609
3	6.454	0.0362	81.201	0.8109	27.648	-7.087	20.561
4	6.574	0.0367	81.198	0.8114	27.220	-5.539	21.681
5	6.678	0.0373	81.196	0.8118	26.805	-7.621	19.184
6	6.788	0.0379	81.193	0.8122	26.403	-6.053	20.350
7	6.894	0.0384	81.191	0.8126	26.013	-5.775	20.237
8	6.996	0.0390	81.189	0.8131	25.633	-6.072	19.562
9	7.111	0.0396	81.186	0.8135	25.265	-2.984	22.281
9.777	7.155	0.0400	81.184	0.8138	24.986	-13.669	11.317
				Average		-6.872	19.789
				Std. Dev.		2.584	2.985

Table F-31
Run 56-2 Chloroform(1) / Acetone(2)
Average Speed: 28488 RPM
T: 26.5° C
x_1^o : 0.05269

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.231	0.0488	81.149	0.8203	20.510		
1	6.303	0.0493	81.146	0.8207	20.274	-4.504	15.770
2	6.376	0.0499	81.144	0.8212	20.043	-3.702	16.341
3	6.446	0.0505	81.142	0.8216	19.817	-3.938	15.880
4	6.518	0.0510	81.139	0.8220	19.596	-3.026	16.570
5	6.584	0.0516	81.137	0.8224	19.380	-4.300	15.081
6	6.650	0.0522	81.135	0.8229	19.169	-3.581	15.589
7	6.715	0.0527	81.133	0.8233	18.963	-3.750	15.212
8	6.779	0.0533	81.130	0.8237	18.760	-3.467	15.293
9	6.844	0.0539	81.128	0.8241	18.562	-3.204	15.358
10	6.906	0.0544	81.126	0.8246	18.369	-3.188	15.181
11	6.968	0.0550	81.124	0.8250	18.179	-3.102	15.077
12	7.028	0.0556	81.121	0.8254	17.993	-3.248	14.745
13	7.086	0.0561	81.119	0.8258	17.811	-3.566	14.244
14	7.136	0.0567	81.117	0.8263	17.632	-5.092	12.540
14.299	7.151	0.0569	81.116	0.8264	17.579	-4.953	12.627
				Average		-3.775	15.034
				Std. Dev.		0.638	1.113

Table F-32
Run 56-3 Chloroform(1) / Acetone(2)
Average Speed: 25944 RPM
T: 26.5° C
x_1^o : 0.05269

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.227	0.0496	81.145	0.8210	20.148		
1	6.325	0.0502	81.143	0.8214	19.920	-3.249	16.671
2	6.412	0.0508	81.141	0.8218	19.697	-4.424	15.274
3	6.505	0.0513	81.138	0.8222	19.479	-3.159	16.320
4	6.593	0.0519	81.136	0.8227	19.266	-3.608	15.657
5	6.676	0.0525	81.134	0.8231	19.057	-4.125	14.931
6	6.760	0.0530	81.131	0.8235	18.853	-3.396	15.457
7	6.843	0.0536	81.129	0.8239	18.653	-3.224	15.428
8	6.925	0.0542	81.127	0.8244	18.457	-3.236	15.221
9	7.004	0.0547	81.125	0.8248	18.265	-3.257	15.008
10	7.078	0.0553	81.122	0.8252	18.078	-3.982	14.095
11	7.148	0.0559	81.120	0.8256	17.894	-4.276	13.617
11.064	7.153	0.0559	81.120	0.8257	17.882	-4.130	13.752
				Average		-3.672	15.119
				Std. Dev.		0.459	0.895

Table F-33
Run 56-1 Chloroform(1) / Acetone(2)
Average Speed: 29475 RPM
T: 37.3° C
x_1^o : 0.05269

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.206	0.0487	82.231	0.8072	20.521		
1	6.278	0.0493	82.228	0.8076	20.283	-4.888	15.396
2	6.353	0.0499	82.226	0.8081	20.051	-4.136	15.915
3	6.417	0.0504	82.223	0.8085	19.824	-5.751	14.073
4	6.486	0.0510	82.221	0.8089	19.602	-4.451	15.152
5	6.556	0.0516	82.218	0.8093	19.386	-4.010	15.376
6	6.620	0.0522	82.216	0.8097	19.173	-4.841	14.332
7	6.686	0.0527	82.213	0.8102	18.966	-4.079	14.887
8	6.748	0.0533	82.210	0.8106	18.763	-4.468	14.294
9	6.813	0.0539	82.208	0.8110	18.564	-3.661	14.903
10	6.874	0.0544	82.206	0.8114	18.369	-4.240	14.130
11	6.937	0.0550	82.203	0.8118	18.179	-3.321	14.857
12	6.996	0.0556	82.201	0.8123	17.992	-4.155	13.837
13	7.055	0.0562	82.198	0.8127	17.809	-3.845	13.964
14	7.108	0.0567	82.196	0.8131	17.630	-4.901	12.729
14.227	7.120	0.0569	82.195	0.8132	17.590	-4.766	12.823
				Average		-4.368	14.444
				Std. Dev.		0.581	0.874

Table F-34

Run 48-1 Chloroform(1) / Acetone(2)
Average Speed: 26005 RPM
T: 26.5° C
x_1^o : 0.06357

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.281	0.0602	81.104	0.8288	16.623		
1	6.363	0.0607	81.101	0.8292	16.467	-2.464	14.003
2	6.437	0.0613	81.099	0.8297	16.314	-3.439	12.875
3	6.514	0.0619	81.097	0.8301	16.165	-2.644	13.520
4	6.589	0.0624	81.095	0.8305	16.017	-2.753	13.265
5	6.660	0.0630	81.093	0.8309	15.873	-3.084	12.789
6	6.730	0.0636	81.090	0.8314	15.731	-3.137	12.594
7	6.801	0.0641	81.088	0.8318	15.591	-2.457	13.134
8	6.877	0.0647	81.086	0.8322	15.454	-1.416	14.039
9	6.942	0.0653	81.084	0.8326	15.320	-3.327	11.993
10	7.009	0.0658	81.082	0.8331	15.188	-2.580	12.607
11	7.073	0.0664	81.080	0.8335	15.058	-2.755	12.302
12	7.138	0.0670	81.077	0.8339	14.930	-2.463	12.467
12.211	7.152	0.0671	81.077	0.8340	14.903	-2.323	12.580
				Average		-2.680	12.936
				Std. Dev.		0.501	0.603

Table F-35
Run 48-2 Chloroform(1) / Acetone(2)
Average Speed: 29502 RPM
T: 26.5° C
x_1^o : 0.06357

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.223	0.0592	81.107	0.8281	16.901		
1	6.292	0.0597	81.105	0.8285	16.740	-1.620	15.120
2	6.355	0.0603	81.103	0.8289	16.582	-2.688	13.894
3	6.415	0.0609	81.101	0.8294	16.427	-3.035	13.393
4	6.478	0.0614	81.099	0.8298	16.275	-2.078	14.197
5	6.544	0.0620	81.096	0.8302	16.126	-1.191	14.935
6	6.602	0.0626	81.094	0.8306	15.980	-2.730	13.250
7	6.659	0.0631	81.092	0.8310	15.836	-2.545	13.291
8	6.716	0.0637	81.090	0.8315	15.695	-2.410	13.285
9	6.774	0.0643	81.088	0.8319	15.556	-2.000	13.556
10	6.831	0.0649	81.085	0.8323	15.419	-1.909	13.511
11	6.888	0.0654	81.083	0.8327	15.285	-1.562	13.724
12	6.945	0.0660	81.081	0.8332	15.154	-1.619	13.534
13	6.998	0.0666	81.079	0.8336	15.024	-2.204	12.820
14	7.050	0.0671	81.077	0.8340	14.897	-1.984	12.913
15	7.100	0.0677	81.075	0.8344	14.772	-2.541	12.231
15.895	7.145	0.0682	81.073	0.8348	14.662	-2.351	12.311
				Average		-2.154	13.498
				Std. Dev.		0.485	0.765

Table F-36
Run 48-3 Chloroform(1) / Acetone(2)
Average Speed: 37016 RPM
T: 26.5° C
x_1^o : 0.06357

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.280	0.0567	81.117	0.8263	17.625		
1	6.322	0.0573	81.115	0.8267	17.451	-2.593	14.858
2	6.362	0.0579	81.112	0.8271	17.279	-3.491	13.788
3	6.400	0.0584	81.110	0.8275	17.111	-3.714	13.397
4	6.439	0.0590	81.108	0.8280	16.946	-3.077	13.869
5	6.478	0.0596	81.106	0.8284	16.784	-2.991	13.793
6	6.516	0.0601	81.104	0.8288	16.626	-2.735	13.891
7	6.554	0.0607	81.101	0.8292	16.470	-2.843	13.627
8	6.590	0.0613	81.099	0.8297	16.317	-3.232	13.086
9	6.627	0.0619	81.097	0.8301	16.167	-2.925	13.242
10	6.661	0.0624	81.095	0.8305	16.020	-3.304	12.716
11	6.697	0.0630	81.093	0.8309	15.876	-2.791	13.084
12	6.732	0.0636	81.090	0.8314	15.734	-2.924	12.809
13	6.767	0.0641	81.088	0.8318	15.594	-2.560	13.035
14	6.802	0.0647	81.086	0.8322	15.457	-2.436	13.021
15	6.836	0.0653	81.084	0.8326	15.322	-2.423	12.899
16	6.869	0.0658	81.082	0.8330	15.190	-2.729	12.461
17	6.907	0.0664	81.080	0.8335	15.060	-0.947	14.113
18	6.936	0.0670	81.077	0.8339	14.932	-3.684	11.248
19	6.971	0.0675	81.075	0.8343	14.806	-1.848	12.959
20	7.002	0.0681	81.073	0.8347	14.683	-2.565	12.118
21	7.035	0.0687	81.071	0.8352	14.561	-2.054	12.507
22	7.066	0.0692	81.069	0.8356	14.442	-2.481	11.961
23	7.097	0.0698	81.067	0.8360	14.324	-2.246	12.078
24	7.127	0.0704	81.065	0.8364	14.208	-2.619	11.590
24.800	7.151	0.0708	81.063	0.8368	14.117	-2.485	11.633
				Average		-2.708	12.951
				Std. Dev.		0.578	0.857

Table F-37
Run 52-1 Chloroform(1) / Acetone(2)
Average Speed: 19149 RPM
T: 26.5° C
x_1^o : 0.08724

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.147	0.0845	81.013	0.8469	11.831		
1	6.267	0.0851	81.011	0.8474	11.752	-1.160	10.592
2	6.375	0.0857	81.009	0.8478	11.674	-1.881	9.793
3	6.482	0.0862	81.007	0.8482	11.597	-1.851	9.746
4	6.592	0.0868	81.005	0.8486	11.521	-1.214	10.307
5	6.695	0.0874	81.004	0.8490	11.446	-1.746	9.700
6	6.796	0.0879	81.002	0.8495	11.372	-1.633	9.739
7	6.897	0.0885	81.000	0.8499	11.299	-1.415	9.883
8	6.994	0.0891	80.998	0.8503	11.227	-1.635	9.592
9	7.078	0.0896	80.996	0.8507	11.155	-2.739	8.417
9.805	7.151	0.0901	80.994	0.8511	11.099	-1.926	9.173
				Average		-1.720	9.694
				Std. Dev.		0.424	0.561

Table F-38
Run 52-2 Chloroform(1) / Acetone(2)
Average Speed: 25953 RPM
T: 26.5° C
x_1^o : 0.08724

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.148	0.0823	81.021	0.8453	12.156		
1	6.214	0.0828	81.019	0.8457	12.072	-1.361	10.711
2	6.276	0.0834	81.017	0.8461	11.990	-1.678	10.312
3	6.338	0.0840	81.015	0.8465	11.909	-1.671	10.238
4	6.397	0.0845	81.013	0.8469	11.829	-1.819	10.010
5	6.458	0.0851	81.011	0.8474	11.750	-1.580	10.170
6	6.517	0.0857	81.009	0.8478	11.672	-1.601	10.071
7	6.576	0.0862	81.007	0.8482	11.595	-1.367	10.228
8	6.630	0.0868	81.005	0.8486	11.519	-2.116	9.403
9	6.686	0.0874	81.003	0.8491	11.444	-1.595	9.849
10	6.740	0.0880	81.001	0.8495	11.370	-1.899	9.471
11	6.796	0.0885	81.000	0.8499	11.297	-1.312	9.985
12	6.851	0.0891	80.998	0.8503	11.225	-1.522	9.703
13	6.904	0.0897	80.996	0.8507	11.154	-1.475	9.678
14	6.957	0.0902	80.994	0.8512	11.083	-1.441	9.643
15	7.009	0.0908	80.992	0.8516	11.014	-1.621	9.393
16	7.058	0.0914	80.990	0.8520	10.945	-1.821	9.124
17	7.105	0.0919	80.988	0.8524	10.878	-2.227	8.651
18	7.149	0.0925	80.986	0.8529	10.811	-2.551	8.260
18.072	7.152	0.0925	80.986	0.8529	10.806	-2.496	8.311
				Average		-1.745	9.643
				Std. Dev.		0.356	0.654

Carbon Tetrachloride / Acetone System

The volume and refractive index properties given in Table F-39 are required to calculate activity coefficient derivatives from ultracentrifuge measurements.

Table F-39
Physical Properties Used With
Carbon Tetrachloride(1) / Acetone(2) Experiments

	Pure Volumes		Excess Volume			Refractive Index		
T	V_1^o	V_2^o	ν_0	ν_1	ν_2	n_A	n_B	n_C
°C	cc/gmol	cc/gmol	cc/gmol					
10	95.5130	72.3434	-0.5148	-0.4118	0.3002	1.36387	0.14080	0
23	97.1490	73.9307	-0.4425	-0.4415	0.2982	1.35734	0.13598	0
26.5	97.3178	74.0957	-0.4425	-0.4415	0.2982	1.35554	0.13466	0
37.3	98.5518	75.3087	-0.2999	-0.4483	0.1409	1.34999	0.13056	0

Sources: v^E: 10° uses a refit of four Handa and Benson (1979) parameters at 10°.
23° and 25° uses Handa and Benson (1979) parameters at 25°.
37.3° uses a refit of four Handa and Benson (1979) parameters at 35°.
V^o: Daubert and Danner (1985).
n: Pure data was interpolated from Loiseleur et al. (1967) and Campbell and Kartzmark (1977). Mixture data is reported in Table 4-6.

The following tables detail the measurements made on the carbon tetrachloride / acetone system.

Table F-40

Run 20-2 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 35568 RPM
T: 23° C
x_1^o : 0.004291

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.361	0.00366	96.565	0.7895	273.545		
1	6.632	0.00404	96.565	0.7899	247.311	-53.003	194.308
2	6.863	0.00443	96.566	0.7903	225.669	-53.060	172.609
3	7.041	0.00482	96.566	0.7907	207.510	-70.262	137.248
3.545	7.138	0.00503	96.566	0.7909	198.797	-58.036	140.761
				Average		-58.590	161.231
				Std. Dev.		7.042	23.547

Table F-41

Run 20-3 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 44862 RPM
T: 23° C
x_1^o : 0.004291

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.352	0.00327	96.565	0.7890	306.043		
1	6.533	0.00366	96.565	0.7895	273.575	-67.643	205.932
2	6.687	0.00404	96.565	0.7899	247.336	-67.137	180.199
3	6.827	0.00443	96.566	0.7903	225.690	-57.321	168.369
4	6.960	0.00482	96.566	0.7907	207.528	-45.139	162.388
5	7.056	0.00521	96.566	0.7911	192.071	-72.093	119.978
5.900	7.143	0.00556	96.566	0.7914	180.009	-58.427	121.582
				Average		-61.293	159.741
				Std. Dev.		8.907	30.743

Table F-42
Run 54-3 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 29490 RPM
T: 10.3° C
x_1^o : 0.02208

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.255	0.0198	94.898	0.8239	50.628		
1	6.332	0.0201	94.898	0.8243	49.686	-10.595	39.091
2	6.411	0.0205	94.899	0.8247	48.779	-7.942	40.837
3	6.487	0.0209	94.899	0.8251	47.904	-7.899	40.005
4	6.558	0.0212	94.899	0.8255	47.059	-9.410	37.650
5	6.640	0.0216	94.899	0.8259	46.244	-2.690	43.554
6	6.709	0.0220	94.900	0.8263	45.457	-7.965	37.492
7	6.779	0.0224	94.900	0.8267	44.696	-6.472	38.224
8	6.850	0.0227	94.900	0.8271	43.960	-4.931	39.029
9	6.917	0.0231	94.900	0.8275	43.248	-5.592	37.656
10	6.984	0.0235	94.901	0.8279	42.559	-5.218	37.340
11	7.047	0.0239	94.901	0.8283	41.891	-5.860	36.031
12	7.108	0.0242	94.901	0.8287	41.244	-6.737	34.507
12.773	7.154	0.0245	94.901	0.8290	40.758	-5.843	34.915
				Average		-6.704	38.179
				Std. Dev.		1.985	2.342

Table F-43
Run 54-1 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 37018 RPM
T: 26.5° C
x_1^o : 0.02208

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.240	0.0185	96.744	0.8032	54.194		
1	6.296	0.0188	96.744	0.8036	53.067	-11.653	41.415
2	6.353	0.0192	96.744	0.8040	51.987	-10.278	41.709
3	6.405	0.0196	96.744	0.8044	50.950	-12.348	38.602
4	6.458	0.0200	96.745	0.8048	49.953	-10.279	39.674
5	6.511	0.0204	96.745	0.8052	48.995	-8.883	40.111
6	6.563	0.0208	96.745	0.8056	48.072	-8.757	39.316
7	6.612	0.0212	96.746	0.8060	47.184	-9.299	37.885
8	6.660	0.0216	96.746	0.8064	46.328	-9.360	36.968
9	6.707	0.0220	96.746	0.8068	45.503	-9.083	36.420
10	6.753	0.0224	96.746	0.8072	44.706	-8.166	36.540
11	6.799	0.0228	96.747	0.8076	43.937	-8.032	35.905
12	6.843	0.0232	96.747	0.8080	43.194	-8.169	35.024
13	6.886	0.0235	96.747	0.8085	42.475	-8.361	34.114
14	6.928	0.0239	96.748	0.8089	41.780	-7.849	33.931
15	6.973	0.0243	96.748	0.8093	41.108	-5.046	36.062
16	7.014	0.0247	96.748	0.8097	40.456	-7.365	33.092
17	7.054	0.0251	96.748	0.8101	39.825	-7.308	32.517
18	7.093	0.0255	96.749	0.8105	39.214	-6.784	32.430
19	7.130	0.0259	96.749	0.8109	38.621	-8.314	30.307
19.515	7.149	0.0261	96.749	0.8111	38.322	-7.867	30.455
				Average		-8.660	36.124
				Std. Dev.		1.603	3.317

Table F-44

Run 54-2 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 29482 RPM
T: 26.5° C
x_1^o : 0.02208

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.236	0.0198	96.745	0.8046	50.528		
1	6.329	0.0202	96.745	0.8050	49.548	-6.554	42.993
2	6.411	0.0206	96.745	0.8054	48.605	-9.707	38.898
3	6.494	0.0210	96.745	0.8058	47.697	-8.321	39.376
4	6.576	0.0214	96.746	0.8062	46.822	-7.291	39.531
5	6.654	0.0217	96.746	0.8066	45.979	-8.341	37.638
6	6.728	0.0221	96.746	0.8070	45.166	-8.795	36.371
7	6.797	0.0225	96.746	0.8074	44.381	-10.027	34.354
8	6.874	0.0229	96.747	0.8078	43.623	-4.930	38.693
9	6.945	0.0233	96.747	0.8082	42.890	-6.699	36.192
10	7.014	0.0237	96.747	0.8086	42.182	-6.957	35.225
11	7.078	0.0241	96.748	0.8090	41.496	-8.333	33.163
12	7.136	0.0245	96.748	0.8094	40.833	-10.196	30.636
12.261	7.152	0.0246	96.748	0.8095	40.663	-9.312	31.351
				Average		-8.113	36.494
				Std. Dev.		1.498	3.395

Table F-45
Run 55-1 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 29497 RPM
T: 26.5° C
x_1^o : 0.07246

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.118	0.0645	96.783	0.8504	15.498		
1	6.149	0.0649	96.784	0.8508	15.404	-2.075	13.329
2	6.179	0.0653	96.784	0.8512	15.312	-2.357	12.955
3	6.207	0.0657	96.784	0.8516	15.221	-3.039	12.182
4	6.236	0.0661	96.785	0.8520	15.131	-2.735	12.395
5	6.264	0.0665	96.785	0.8524	15.042	-2.731	12.310
6	6.291	0.0669	96.786	0.8528	14.953	-3.077	11.877
7	6.319	0.0673	96.786	0.8532	14.866	-2.606	12.260
8	6.347	0.0677	96.786	0.8536	14.780	-2.705	12.075
9	6.374	0.0680	96.787	0.8540	14.695	-2.707	11.989
10	6.399	0.0684	96.787	0.8544	14.611	-3.441	11.170
11	6.425	0.0688	96.788	0.8548	14.528	-2.981	11.547
12	6.451	0.0692	96.788	0.8552	14.446	-2.658	11.788
13	6.478	0.0696	96.788	0.8556	14.365	-2.205	12.160
14	6.504	0.0700	96.789	0.8560	14.284	-2.893	11.391
15	6.529	0.0704	96.789	0.8564	14.205	-2.609	11.596
16	6.555	0.0708	96.790	0.8568	14.126	-2.423	11.703
17	6.581	0.0712	96.790	0.8572	14.049	-2.216	11.832
18	6.604	0.0716	96.790	0.8576	13.972	-3.569	10.403
19	6.630	0.0720	96.791	0.8580	13.896	-2.183	11.713
20	6.654	0.0724	96.791	0.8584	13.820	-2.829	10.991
21	6.678	0.0727	96.792	0.8587	13.746	-2.753	10.993
22	6.702	0.0731	96.792	0.8591	13.672	-2.253	11.420
23	6.726	0.0735	96.792	0.8595	13.600	-2.565	11.035
24	6.750	0.0739	96.793	0.8599	13.528	-2.567	10.961
25	6.773	0.0743	96.793	0.8603	13.456	-2.624	10.833
26	6.797	0.0747	96.794	0.8607	13.386	-2.242	11.144
27	6.820	0.0751	96.794	0.8611	13.316	-2.700	10.616
28	6.843	0.0755	96.795	0.8615	13.247	-2.418	10.829
29	6.866	0.0759	96.795	0.8619	13.179	-2.329	10.849
30	6.889	0.0763	96.795	0.8623	13.111	-2.209	10.901
31	6.911	0.0767	96.796	0.8627	13.044	-2.346	10.698
32	6.934	0.0771	96.796	0.8631	12.978	-2.410	10.568
33	6.957	0.0774	96.797	0.8635	12.912	-1.932	10.980
34	6.978	0.0778	96.797	0.8639	12.847	-2.562	10.285
35	7.000	0.0782	96.797	0.8643	12.783	-2.301	10.482
36	7.021	0.0786	96.798	0.8646	12.719	-2.498	10.222

Table F-45 Continued

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
37	7.043	0.0790	96.798	0.8650	12.656	-2.209	10.447
38	7.064	0.0794	96.799	0.8654	12.594	-2.576	10.017
39	7.085	0.0798	96.799	0.8658	12.532	-2.362	10.170
40	7.106	0.0802	96.800	0.8662	12.471	-2.114	10.356
41	7.127	0.0806	96.800	0.8666	12.410	-2.314	10.096
42	7.149	0.0810	96.800	0.8670	12.350	-1.837	10.513
42.096	7.149	0.0810	96.801	0.8670	12.344	-9.567	2.777
				Average		-2.691	11.043
				Std. Dev.		1.118	1.500

Table F-46
Run 55-2 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 21724 RPM
T: 26.5° C
x_1^o : 0.07246

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.115	0.0679	96.787	0.8539	14.717		
1	6.164	0.0683	96.787	0.8543	14.633	-3.297	11.336
2	6.213	0.0687	96.787	0.8547	14.549	-3.287	11.262
3	6.262	0.0691	96.788	0.8551	14.467	-2.874	11.593
4	6.311	0.0695	96.788	0.8555	14.385	-2.921	11.464
5	6.359	0.0699	96.789	0.8559	14.305	-2.840	11.465
6	6.406	0.0703	96.789	0.8563	14.225	-3.018	11.207
7	6.452	0.0707	96.790	0.8567	14.146	-3.079	11.067
8	6.499	0.0711	96.790	0.8571	14.068	-2.606	11.462
9	6.544	0.0715	96.790	0.8575	13.991	-2.980	11.011
10	6.591	0.0719	96.791	0.8579	13.915	-2.457	11.458
11	6.633	0.0723	96.791	0.8583	13.840	-3.457	10.382
12	6.677	0.0726	96.792	0.8586	13.765	-2.701	11.064
13	6.721	0.0730	96.792	0.8590	13.691	-2.763	10.928
14	6.764	0.0734	96.792	0.8594	13.618	-2.715	10.903
15	6.806	0.0738	96.793	0.8598	13.546	-2.876	10.670
16	6.849	0.0742	96.793	0.8602	13.474	-2.562	10.913
17	6.891	0.0746	96.794	0.8606	13.404	-2.738	10.665
18	6.932	0.0750	96.794	0.8610	13.334	-2.666	10.668
19	6.973	0.0754	96.794	0.8614	13.264	-2.690	10.574
20	7.014	0.0758	96.795	0.8618	13.196	-2.478	10.718
21	7.054	0.0762	96.795	0.8622	13.128	-2.763	10.365
22	7.093	0.0766	96.796	0.8626	13.061	-2.801	10.260
23	7.132	0.0770	96.796	0.8630	12.994	-2.466	10.528
23.421	7.149	0.0771	96.796	0.8631	12.967	-2.428	10.538
				Average		-2.811	10.938
				Std. Dev.		0.267	0.394

Table F-47
Run 55-3 Carbon Tetrachloride(1) / Acetone(2)
Average Speed: 21720 RPM
T: 26.5° C
x_1^o : 0.07246

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.097	0.0679	98.070	0.8403	14.737		
1	6.149	0.0683	98.071	0.8407	14.650	-3.364	11.286
2	6.188	0.0687	98.072	0.8411	14.563	-6.012	8.551
3	6.252	0.0691	98.072	0.8415	14.478	-0.534	13.945
4	6.301	0.0695	98.073	0.8419	14.394	-3.449	10.945
5	6.350	0.0699	98.074	0.8423	14.311	-3.406	10.904
6	6.398	0.0703	98.075	0.8427	14.229	-3.591	10.638
7	6.446	0.0707	98.075	0.8431	14.147	-3.243	10.905
8	6.494	0.0711	98.076	0.8435	14.067	-3.255	10.812
9	6.541	0.0715	98.077	0.8439	13.987	-3.215	10.772
10	6.586	0.0719	98.077	0.8443	13.909	-3.379	10.529
11	6.632	0.0723	98.078	0.8447	13.831	-3.210	10.621
12	6.676	0.0727	98.079	0.8451	13.754	-3.549	10.206
13	6.720	0.0731	98.080	0.8455	13.678	-3.189	10.490
14	6.765	0.0735	98.080	0.8459	13.603	-3.109	10.494
15	6.810	0.0739	98.081	0.8463	13.529	-2.903	10.626
16	6.853	0.0743	98.082	0.8467	13.455	-3.108	10.347
17	6.895	0.0747	98.083	0.8471	13.383	-3.137	10.246
18	6.938	0.0751	98.083	0.8475	13.311	-3.024	10.287
19	6.980	0.0755	98.084	0.8479	13.239	-3.117	10.122
20	7.021	0.0759	98.085	0.8483	13.169	-3.003	10.166
21	7.063	0.0763	98.085	0.8487	13.099	-2.910	10.189
22	7.103	0.0767	98.086	0.8491	13.030	-3.076	9.955
23	7.144	0.0771	98.087	0.8495	12.962	-2.820	10.142
23.196	7.151	0.0772	98.087	0.8496	12.949	-3.080	9.869
				Average		-3.195	10.544
				Std. Dev.		0.814	0.875

Benzene / Acetonitrile System

The volume and refractive index properties given in Table F-48 are required to calculate activity coefficient derivatives from ultracentrifuge measurements.

Table F-48
Physical Properties Used With
Benzene(1) / Acetonitrile (2) Experiments

	Pure Volumes		Excess Volume			Refractive Index		
T	V_1^o	V_2^o	ν_0	ν_1	ν_2	n_A	n_B	n_C
°C	cc/gmol	cc/gmol	cc/gmol					
26.5	89.65521	52.78436	-0.307	0.91	0	1.3416	0.24642	-0.1345
37.3	90.76987	53.56951	-0.307	0.91	0	1.3416	0.24284	-0.1360

Sources: v^E: 26.5° and 37.3° use Handa and Benson (1979) parameters at 30° directly.
V^o: Daubert and Danner (1985).
n: Pure data is at 25° from Daubert and Danner (1985). Mixture data is reported in Table 4-8.

The following tables detail the measurements made on the benzene / acetonitrile system.

Table F-49

Run 43-1 Benzene(1) / Acetonitrile(2)
Average Speed: 39445 RPM
T: 26.5° C
x_1^o : 0.02271

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.408	0.0224	90.154	0.7811	44.740		
1	6.642	0.0226	90.153	0.7811	44.305	-8.332	35.973
2	6.853	0.0228	90.152	0.7811	43.878	-10.302	33.576
3	7.065	0.0230	90.151	0.7812	43.460	-8.476	34.983
3.361	7.142	0.0231	90.150	0.7812	43.311	-7.251	36.059
				Average		-8.590	35.148
				Std. Dev.		1.096	1.001

Table F-50

Run 43-2 Benzene(1) / Acetonitrile(2)
Average Speed: 42037 RPM
T: 26.5° C
x_1^o : 0.02271

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.408	0.0223	90.154	0.7810	44.832		
1	6.620	0.0225	90.153	0.7811	44.396	-7.434	36.962
2	6.800	0.0227	90.152	0.7811	43.967	-11.362	32.606
3	6.996	0.0230	90.151	0.7811	43.547	-7.250	36.297
3.752	7.143	0.0231	90.150	0.7812	43.236	-5.910	37.326
				Average		-7.989	35.798
				Std. Dev.		2.034	1.880

Table F-51

Run 42-1 Benzene(1) / Acetonitrile(2)
Average Speed: 31418 RPM
T: 26.5° C
x_1^o : 0.037474

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.698	0.0373	90.088	0.7832	26.841		
1	6.952	0.0375	90.087	0.7833	26.681	-1.666	25.015
1.977	7.157	0.0377	90.087	0.7833	26.527	-5.134	21.393
				Average		-3.400	23.204
				Std. Dev.		1.734	1.811

Table F-52
Run 42-3 Benzene(1) / Acetonitrile(2)
Average Speed: 35526 RPM
T: 26.5° C
x_1^o : 0.037474

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.684	0.0371	90.089	0.7832	26.953		
1	6.821	0.0373	90.088	0.7832	26.792	-9.516	17.275
2	6.966	0.0375	90.087	0.7833	26.633	-8.072	18.561
3	7.100	0.0378	90.086	0.7833	26.475	-8.965	17.510
3.289	7.138	0.0378	90.086	0.7833	26.430	-8.588	17.842
				Average		-8.785	17.797
				Std. Dev.		0.528	0.485

Table F-53
Run 57-1 Benzene(1) / Acetonitrile(2)
Average Speed: 31401 RPM
T: 26.5° C
x_1^o : 0.042546

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.106	0.0419	90.069	0.7839	23.844		
1	6.315	0.0422	90.068	0.7839	23.717	-5.156	18.560
2	6.498	0.0424	90.067	0.7840	23.591	-6.801	16.790
3	6.710	0.0426	90.066	0.7840	23.467	-3.504	19.963
4	6.910	0.0428	90.065	0.7840	23.344	-3.871	19.473
5	7.076	0.0431	90.064	0.7841	23.222	-6.641	16.581
5.501	7.159	0.0432	90.063	0.7841	23.162	-6.189	16.973
				Average		-5.360	18.057
				Std. Dev.		1.298	1.345

Table F-54
Run 57-2 Benzene(1) / Acetonitrile(2)
Average Speed: 42193 RPM
T: 26.5° C
x_1^o : 0.042546

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.126	0.0412	90.072	0.7838	24.266		
1	6.204	0.0414	90.071	0.7838	24.135	-11.506	12.628
2	6.297	0.0417	90.070	0.7839	24.005	-8.907	15.098
3	6.386	0.0419	90.069	0.7839	23.876	-9.162	14.714
4	6.479	0.0421	90.068	0.7839	23.749	-8.141	15.608
5	6.570	0.0423	90.067	0.7840	23.623	-8.142	15.481
6	6.664	0.0426	90.066	0.7840	23.499	-7.334	16.165
7	6.751	0.0428	90.065	0.7840	23.375	-8.129	15.246
8	6.839	0.0430	90.064	0.7841	23.253	-7.740	15.513
9	6.927	0.0432	90.063	0.7841	23.133	-7.385	15.748
10	7.013	0.0435	90.062	0.7841	23.013	-7.394	15.619
11	7.094	0.0437	90.061	0.7842	22.895	-8.125	14.769
11.801	7.159	0.0439	90.061	0.7842	22.801	-7.869	14.932
				Average		-8.320	15.127
				Std. Dev.		1.103	0.857

Table F-55
Run 57-3 Benzene(1) / Acetonitrile(2)
Average Speed: 42004 RPM
T: 37.3° C
x_1^o : 0.042546

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.091	0.0412	91.186	0.7724	24.281		
1	6.190	0.0414	91.185	0.7725	24.147	-8.818	15.329
2	6.276	0.0416	91.184	0.7725	24.015	-10.710	13.305
3	6.370	0.0419	91.184	0.7725	23.885	-8.953	14.932
4	6.460	0.0421	91.183	0.7726	23.755	-9.268	14.488
5	6.551	0.0423	91.182	0.7726	23.627	-8.783	14.844
6	6.644	0.0426	91.181	0.7726	23.501	-8.135	15.366
7	6.732	0.0428	91.180	0.7727	23.376	-8.700	14.676
8	6.827	0.0430	91.179	0.7727	23.252	-7.129	16.123
9	6.902	0.0432	91.178	0.7727	23.129	-10.251	12.878
10	7.001	0.0435	91.177	0.7728	23.007	-5.878	17.130
11	7.084	0.0437	91.176	0.7728	22.887	-8.240	14.647
12	7.163	0.0439	91.175	0.7728	22.768	-8.730	14.038
11.949	7.159	0.0439	91.175	0.7728	22.774	-8.581	14.193
				Average		-8.629	14.765
				Std. Dev.		1.169	1.067

Table F-56
Run 58-2 Benzene(1) / Acetonitrile(2)
Average Speed: 42007 RPM
T: 26.5° C
x_1^o : 0.056216

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.163	0.0546	90.016	0.7857	18.312		
1	6.243	0.0548	90.016	0.7858	18.236	-5.839	12.397
2	6.314	0.0551	90.015	0.7858	18.161	-6.981	11.180
3	6.388	0.0553	90.014	0.7858	18.086	-6.259	11.827
4	6.459	0.0555	90.013	0.7859	18.012	-6.651	11.361
5	6.530	0.0557	90.012	0.7859	17.938	-6.477	11.461
6	6.597	0.0560	90.011	0.7859	17.865	-6.797	11.068
7	6.673	0.0562	90.010	0.7859	17.793	-5.220	12.572
8	6.743	0.0564	90.009	0.7860	17.721	-6.043	11.678
9	6.807	0.0567	90.008	0.7860	17.649	-6.733	10.917
10	6.881	0.0569	90.007	0.7860	17.579	-4.945	12.633
11	6.947	0.0571	90.006	0.7861	17.508	-6.212	11.296
12	7.011	0.0573	90.006	0.7861	17.439	-6.317	11.121
13	7.077	0.0576	90.005	0.7861	17.369	-5.732	11.637
14	7.139	0.0578	90.004	0.7862	17.301	-6.341	10.960
14.269	7.156	0.0579	90.003	0.7862	17.282	-6.230	11.053
				Average		-6.185	11.544
				Std. Dev.		0.546	0.559

Table F-57
Run 58-3 Benzene(1) / Acetonitrile(2)
Average Speed: 31386 RPM
T: 26.5° C
x_1^o : 0.056216

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.162	0.0554	90.013	0.7858	18.056		
1	6.306	0.0556	90.012	0.7859	17.982	-5.484	12.498
2	6.441	0.0558	90.012	0.7859	17.908	-5.974	11.934
3	6.582	0.0561	90.011	0.7859	17.835	-5.125	12.710
4	6.725	0.0563	90.010	0.7860	17.763	-4.566	13.197
5	6.864	0.0565	90.009	0.7860	17.691	-4.543	13.148
6	6.991	0.0568	90.008	0.7860	17.620	-5.435	12.185
7	7.111	0.0570	90.007	0.7861	17.550	-5.789	11.761
7.383	7.157	0.0571	90.007	0.7861	17.523	-5.563	11.960
				Average		-5.310	12.424
				Std. Dev.		0.494	0.520

Table F-58
Run 58-1 Benzene(1) / Acetonitrile(2)
Average Speed: 41946 RPM
T: 37.3° C
x_1^o : 0.056216

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.149	0.0545	91.131	0.7744	18.333		
1	6.224	0.0548	91.130	0.7744	18.256	-7.118	11.137
2	6.296	0.0550	91.130	0.7744	18.179	-7.162	11.016
3	6.370	0.0552	91.129	0.7745	18.103	-6.810	11.293
4	6.442	0.0555	91.128	0.7745	18.027	-6.928	11.099
5	6.510	0.0557	91.127	0.7745	17.952	-7.229	10.723
6	6.579	0.0559	91.126	0.7746	17.878	-6.925	10.953
7	6.654	0.0562	91.125	0.7746	17.804	-5.907	11.897
8	6.731	0.0564	91.124	0.7746	17.731	-5.296	12.435
9	6.794	0.0566	91.123	0.7747	17.658	-7.327	10.332
10	6.862	0.0569	91.122	0.7747	17.586	-6.348	11.238
11	6.932	0.0571	91.121	0.7747	17.515	-5.907	11.608
12	6.995	0.0573	91.120	0.7748	17.444	-6.820	10.624
13	7.059	0.0576	91.119	0.7748	17.374	-6.520	10.854
14	7.123	0.0578	91.118	0.7748	17.304	-6.406	10.898
14.518	7.156	0.0579	91.118	0.7748	17.268	-6.276	10.992
				Average		-6.599	11.140
				Std. Dev.		0.85	0.5

Table F-59

Run 41-2 Benzene(1) / Acetonitrile(2)
Average Speed: 25912 RPM
T: 26.5° C
x_1^o : 0.058205

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.582	0.0579	90.003	0.7862	17.261		
1	6.848	0.0582	90.002	0.7862	17.193	-0.490	16.703
2	7.049	0.0584	90.001	0.7863	17.126	-4.055	13.071
2.674	7.156	0.0585	90.001	0.7863	17.081	-6.508	10.573
				Average		-3.685	13.449
				Std. Dev.		2.471	2.517

Table F-60

Run 45-1 Benzene(1) / Acetonitrile(2)
Average Speed: 31407 RPM
T: 26.5° C
x_1^o : 0.064272

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.678	0.0639	89.980	0.7870	15.657		
1	6.834	0.0641	89.979	0.7871	15.601	-1.271	14.330
2	6.967	0.0643	89.978	0.7871	15.545	-3.021	12.525
3	7.083	0.0646	89.977	0.7871	15.490	-4.315	11.175
3.878	7.159	0.0648	89.976	0.7872	15.441	-7.027	8.415
				Average		-3.908	11.611
				Std. Dev.		2.100	2.158

Table F-61
Run 45-2 Benzene(1) / Acetonitrile(2)
Average Speed: 35533 RPM
T: 26.5° C
x_1^o : 0.064272

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.671	0.0637	89.980	0.7870	15.690		
1	6.788	0.0640	89.980	0.7870	15.634	-1.907	13.727
2	6.886	0.0642	89.979	0.7871	15.578	-3.868	11.709
3	6.989	0.0644	89.978	0.7871	15.522	-3.038	12.484
4	7.088	0.0647	89.977	0.7871	15.467	-3.253	12.214
4.777	7.160	0.0648	89.976	0.7872	15.424	-3.905	11.519
				Average		-3.194	12.331
				Std. Dev.		0.727	0.779

Table F-62
Run 44-1 Benzene(1) / Acetonitrile(2)
Average Speed: 25950 RPM
T: 26.5° C
x_1^o : 0.086099

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.772	0.0858	89.898	0.7901	11.659		
1	6.911	0.0860	89.897	0.7901	11.627	-3.284	8.343
2	7.050	0.0862	89.897	0.7902	11.595	-3.073	8.522
2.819	7.151	0.0864	89.896	0.7902	11.569	-3.799	7.770
				Average		-3.385	8.212
				Std. Dev.		0.305	0.321

Carbon Tetrachloride / Methanol System

The volume and refractive index properties given in Table F-63 are required to calculate activity coefficient derivatives from ultracentrifuge measurements.

Table F-63
Physical Properties Used With
Carbon Tetrachloride(1) / Methanol(2) Experiments

T	Pure Volumes		Excess Volume			Refractive Index		
	V_1^o	V_2^o	ν_0	ν_1	ν_2	n_A	n_B	n_C
°C	cc/gmol	cc/gmol	cc/gmol					
26.5	97.3178	40.77289	-0.1567	0.2999	0.1285	1.32652	0.31253	-0.3165
37.3	98.55184	41.29302	-0.1567	0.2999	0.1285	1.32652	0.29958	-0.2546

Sources: v^E: 26.5° and 37.3° uses a refit of four Handa and Benson (1979) parameters at 25°.

V^o: Daubert and Danner (1985).

n: Pure data is at 25° from Daubert and Danner (1985). Mixture data is reported in Table 4-10.

The following tables detail the measurements made on the carbon tetrachloride / methanol system.

Table F-64

Run 60-2 Carbon Tetrachloride(1) / Methanol(2)

Average Speed: 21727 RPM

T: 26.5° C

x_1^o : 0.019232

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.174	0.0181	97.005	0.8194	55.364		
1	6.257	0.0182	97.005	0.8197	54.832	-9.502	45.330
2	6.337	0.0184	97.005	0.8200	54.310	-9.983	44.327
3	6.420	0.0186	97.005	0.8204	53.798	-7.905	45.893
4	6.493	0.0188	97.006	0.8207	53.295	-11.688	41.607
5	6.567	0.0189	97.006	0.8210	52.802	-10.849	41.953
6	6.641	0.0191	97.006	0.8213	52.317	-9.915	42.401
7	6.713	0.0193	97.006	0.8216	51.841	-9.523	42.318
8	6.782	0.0195	97.006	0.8219	51.373	-10.692	40.681
9	6.851	0.0196	97.006	0.8223	50.913	-10.080	40.834
10	6.918	0.0198	97.006	0.8226	50.462	-10.431	40.031
11	6.986	0.0200	97.007	0.8229	50.018	-8.721	41.298
12	7.047	0.0202	97.007	0.8232	49.582	-12.606	36.976
13	7.107	0.0203	97.007	0.8235	49.153	-12.027	37.126
13.800	7.155	0.0205	97.007	0.8238	48.815	-11.397	37.418
				Average		-10.380	41.299
				Std. Dev.		1.241	2.708

Table F-65

Run 60-3 Carbon Tetrachloride(1) / Methanol(2)

Average Speed: 25971 RPM

T: 26.5° C

x_1^o : 0.019232

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.174	0.0176	97.005	0.8185	56.856		
1	6.239	0.0178	97.005	0.8189	56.295	-5.528	50.767
2	6.299	0.0179	97.005	0.8192	55.746	-8.727	47.020
3	6.354	0.0181	97.005	0.8195	55.207	-11.844	43.363
4	6.408	0.0183	97.005	0.8198	54.678	-11.352	43.326
5	6.462	0.0185	97.005	0.8201	54.159	-10.070	44.089
6	6.516	0.0186	97.005	0.8204	53.650	-10.335	43.314
7	6.566	0.0188	97.006	0.8208	53.150	-11.648	41.501
8	6.619	0.0190	97.006	0.8211	52.659	-9.173	43.486
9	6.672	0.0192	97.006	0.8214	52.177	-8.261	43.916
10	6.720	0.0193	97.006	0.8217	51.703	-11.227	40.476
11	6.771	0.0195	97.006	0.8220	51.238	-8.654	42.584
12	6.818	0.0197	97.006	0.8224	50.780	-10.894	39.887
13	6.865	0.0199	97.006	0.8227	50.331	-10.061	40.270
14	6.913	0.0200	97.007	0.8230	49.890	-9.135	40.755
15	6.960	0.0202	97.007	0.8233	49.456	-9.118	40.337
16	7.003	0.0204	97.007	0.8236	49.029	-11.228	37.801
17	7.047	0.0206	97.007	0.8239	48.609	-10.541	38.068
18	7.090	0.0207	97.007	0.8243	48.197	-10.682	37.515
19	7.135	0.0209	97.007	0.8246	47.791	-7.900	39.891
19.452	7.155	0.0210	97.007	0.8247	47.610	-7.483	40.127
				Average		-9.693	41.925
				Std. Dev.		1.584	3.109

Table F-66
Run 60-1 Carbon Tetrachloride(1) / Methanol(2)
Average Speed: 21722 RPM
T: 37.3° C
x_1^o : 0.019232

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.163	0.0183	98.239	0.8094	54.792		
1	6.276	0.0184	98.239	0.8097	54.252	2.793	57.045
2	6.392	0.0186	98.239	0.8101	53.722	5.573	59.295
3	6.494	0.0188	98.240	0.8104	53.202	0.077	53.280
4	6.582	0.0190	98.240	0.8107	52.692	-5.784	46.909
5	6.670	0.0192	98.240	0.8110	52.192	-4.942	47.250
6	6.753	0.0193	98.240	0.8114	51.701	-6.168	45.533
7	6.828	0.0195	98.240	0.8117	51.219	-9.987	41.232
8	6.903	0.0197	98.240	0.8120	50.746	-9.352	41.394
9	6.971	0.0199	98.241	0.8123	50.281	-11.902	38.379
10	7.040	0.0201	98.241	0.8127	49.824	-10.668	39.156
11	7.104	0.0203	98.241	0.8130	49.376	-12.391	36.985
11.838	7.159	0.0204	98.241	0.8133	49.006	-11.706	37.300
				Average		-6.205	45.313
				Std. Dev.		5.817	7.385

Table F-67
Run 61-1 Carbon Tetrachloride(1) / Methanol(2)
Average Speed: 21741 RPM
T: 26.5° C
x_1^o : 0.034377

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.083	0.0322	97.017	0.8445	31.099		
1	6.131	0.0323	97.017	0.8448	30.926	-7.099	23.827
2	6.178	0.0325	97.017	0.8451	30.754	-6.627	24.127
3	6.234	0.0327	97.018	0.8454	30.584	-1.933	28.652
4	6.293	0.0329	97.018	0.8457	30.416	-0.183	30.233
5	6.347	0.0331	97.018	0.8460	30.250	-2.068	28.182
6	6.397	0.0332	97.018	0.8463	30.085	-4.086	25.999
7	6.442	0.0334	97.018	0.8467	29.922	-6.014	23.908
8	6.488	0.0336	97.018	0.8470	29.761	-5.623	24.138
9	6.532	0.0338	97.019	0.8473	29.601	-5.998	23.603
10	6.573	0.0340	97.019	0.8476	29.444	-7.213	22.231
11	6.612	0.0341	97.019	0.8479	29.287	-8.107	21.180
12	6.651	0.0343	97.019	0.8482	29.133	-8.063	21.069
13	6.692	0.0345	97.019	0.8485	28.979	-7.041	21.938
14	6.727	0.0347	97.019	0.8489	28.828	-9.164	19.664
15	6.765	0.0349	97.020	0.8492	28.678	-8.161	20.517
16	6.802	0.0351	97.020	0.8495	28.529	-8.006	20.524
17	6.837	0.0352	97.020	0.8498	28.382	-9.029	19.353
18	6.871	0.0354	97.020	0.8501	28.237	-9.007	19.230
19	6.906	0.0356	97.020	0.8504	28.092	-8.607	19.486
20	6.939	0.0358	97.020	0.8508	27.949	-9.254	18.696
21	6.971	0.0360	97.020	0.8511	27.808	-9.423	18.385
22	7.003	0.0361	97.021	0.8514	27.668	-9.494	18.174
23	7.034	0.0363	97.021	0.8517	27.529	-10.367	17.162
24	7.063	0.0365	97.021	0.8520	27.392	-10.540	16.852
25	7.091	0.0367	97.021	0.8523	27.256	-11.043	16.213
26	7.119	0.0369	97.021	0.8526	27.121	-11.076	16.045
27	7.148	0.0371	97.021	0.8529	26.988	-10.086	16.901
27.135	7.152	0.0371	97.021	0.8530	26.970	-10.005	16.964
				Average		-7.619	21.188
				Std. Dev.		2.745	3.816

Table F-68
Run 59-1 Carbon Tetrachloride(1) / Methanol(2)
Average Speed: 17959 RPM
T: 26.5° C
x_1^o : 0.049133

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.273	0.0473	97.031	0.8704	21.139		
1	6.328	0.0475	97.031	0.8707	21.056	-2.771	18.285
2	6.380	0.0477	97.031	0.8710	20.974	-3.751	17.223
3	6.429	0.0479	97.031	0.8713	20.892	-4.433	16.459
4	6.477	0.0481	97.031	0.8716	20.811	-4.670	16.141
5	6.523	0.0482	97.031	0.8719	20.730	-4.901	15.829
6	6.570	0.0484	97.032	0.8722	20.650	-4.661	15.989
7	6.618	0.0486	97.032	0.8726	20.570	-4.047	16.524
8	6.663	0.0488	97.032	0.8729	20.491	-4.805	15.687
9	6.707	0.0490	97.032	0.8732	20.413	-5.279	15.135
10	6.750	0.0492	97.032	0.8735	20.335	-5.042	15.293
11	6.791	0.0494	97.032	0.8738	20.258	-5.736	14.522
12	6.831	0.0496	97.033	0.8741	20.181	-5.945	14.236
13	6.873	0.0497	97.033	0.8744	20.105	-5.277	14.828
14	6.914	0.0499	97.033	0.8747	20.030	-5.493	14.536
15	6.953	0.0501	97.033	0.8751	19.955	-5.787	14.168
16	6.992	0.0503	97.033	0.8754	19.880	-5.812	14.068
17	7.028	0.0505	97.033	0.8757	19.806	-6.466	13.340
18	7.064	0.0507	97.034	0.8760	19.733	-6.609	13.123
19	7.100	0.0509	97.034	0.8763	19.660	-6.574	13.086
20	7.133	0.0511	97.034	0.8766	19.587	-7.302	12.285
20.680	7.156	0.0512	97.034	0.8768	19.538	-7.204	12.335
				Average		-5.360	14.909
				Std. Dev.		1.108	1.552

Table F-69

Run 59-3 Carbon Tetrachloride(1) / Methanol(2)
Average Speed: 21744 RPM
T: 26.5° C
x_1^o : 0.049133

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.275	0.0464	97.030	0.8688	21.569		
1	6.311	0.0465	97.030	0.8691	21.483	-3.840	17.643
2	6.345	0.0467	97.030	0.8694	21.397	-4.675	16.722
3	6.378	0.0469	97.030	0.8697	21.312	-5.174	16.139
4	6.410	0.0471	97.030	0.8700	21.228	-5.328	15.900
5	6.442	0.0473	97.030	0.8703	21.144	-5.361	15.783
6	6.473	0.0475	97.031	0.8707	21.061	-5.484	15.577
7	6.505	0.0477	97.031	0.8710	20.979	-5.154	15.824
8	6.535	0.0479	97.031	0.8713	20.897	-5.740	15.156
9	6.566	0.0480	97.031	0.8716	20.815	-5.415	15.400
10	6.596	0.0482	97.031	0.8719	20.735	-5.446	15.289
11	6.626	0.0484	97.031	0.8722	20.655	-5.302	15.352
12	6.656	0.0486	97.032	0.8725	20.575	-5.578	14.997
13	6.685	0.0488	97.032	0.8729	20.496	-5.446	15.050
14	6.714	0.0490	97.032	0.8732	20.418	-5.628	14.789
15	6.744	0.0492	97.032	0.8735	20.340	-5.041	15.299
16	6.771	0.0494	97.032	0.8738	20.263	-6.236	14.026
17	6.797	0.0495	97.033	0.8741	20.186	-6.517	13.669
18	6.826	0.0497	97.033	0.8744	20.110	-5.323	14.787
19	6.852	0.0499	97.033	0.8747	20.034	-6.091	13.943
20	6.879	0.0501	97.033	0.8750	19.959	-5.883	14.076
21	6.906	0.0503	97.033	0.8754	19.885	-5.808	14.077
22	6.933	0.0505	97.033	0.8757	19.811	-5.716	14.095
23	6.959	0.0507	97.034	0.8760	19.737	-6.125	13.612
24	6.984	0.0509	97.034	0.8763	19.664	-6.307	13.357
25	7.009	0.0510	97.034	0.8766	19.592	-6.302	13.289
26	7.034	0.0512	97.034	0.8769	19.520	-6.237	13.282
27	7.058	0.0514	97.034	0.8772	19.448	-6.217	13.231
28	7.083	0.0516	97.034	0.8775	19.377	-6.346	13.031
29	7.106	0.0518	97.035	0.8779	19.307	-7.049	12.258
30	7.128	0.0520	97.035	0.8782	19.237	-7.093	12.144
31	7.149	0.0522	97.035	0.8785	19.167	-7.852	11.315
31.241	7.154	0.0522	97.035	0.8786	19.150	-7.807	11.344
				Average		-5.860	14.389
				Std. Dev.		0.818	1.466

Table F-70
Run 59-4 Carbon Tetrachloride(1) / Methanol(2)
Average Speed: 17970 RPM
T: 37.3° C
x_1^o : 0.049133

Fringe No. j	r cm	x_1	$\overline{V}_1$ cc/gmole	ρ g/cc	$1/x_1$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)$	$\left(\frac{\partial \mu_1}{\partial x_1}\right)/RT$
0	6.264	0.0472	98.264	0.8593	21.176		
1	6.316	0.0474	98.265	0.8596	21.091	-4.972	16.119
2	6.368	0.0476	98.265	0.8599	21.006	-4.767	16.239
3	6.416	0.0478	98.265	0.8602	20.922	-5.691	15.230
4	6.464	0.0480	98.265	0.8605	20.838	-5.597	15.242
5	6.509	0.0482	98.265	0.8609	20.755	-6.152	14.603
6	6.555	0.0484	98.265	0.8612	20.673	-5.986	14.687
7	6.600	0.0486	98.266	0.8615	20.592	-5.870	14.721
8	6.646	0.0488	98.266	0.8618	20.510	-5.454	15.056
9	6.690	0.0489	98.266	0.8621	20.430	-5.959	14.471
10	6.734	0.0491	98.266	0.8624	20.350	-5.872	14.479
11	6.777	0.0493	98.266	0.8628	20.271	-6.116	14.155
12	6.818	0.0495	98.267	0.8631	20.192	-6.322	13.871
13	6.859	0.0497	98.267	0.8634	20.114	-6.387	13.727
14	6.900	0.0499	98.267	0.8637	20.037	-6.164	13.872
15	6.941	0.0501	98.267	0.8640	19.960	-6.298	13.662
16	6.980	0.0503	98.267	0.8643	19.883	-6.483	13.400
17	7.017	0.0505	98.267	0.8647	19.808	-7.043	12.765
18	7.056	0.0507	98.268	0.8650	19.732	-6.516	13.216
19	7.093	0.0509	98.268	0.8653	19.658	-6.839	12.818
20	7.126	0.0511	98.268	0.8656	19.583	-8.057	11.526
20.883	7.155	0.0512	98.268	0.8659	19.518	-7.947	11.571
				Average		-6.214	14.068
				Std. Dev.		0.785	1.226

APPENDIX G

FORTRAN PROGRAMS FOR THE CALCULATION FOR PVT CALCULATIONS AND DATA REGRESSION

PVT Calculations

The FORTRAN program PVTKT was written to calculate volumes and isothermal compressibilities from the equation of state of Huang (1986). Using equation (5-19) the program will calculate the volume, V, given a temperature, T, and pressure P. A reference pressure and volume must also be specified at the same temperature. The program will also use equation (5-21) to calculate the compressibility, κ_T. If the user supplies volume data, the compressibility will be calculated using both the calculated volume and the user supplied volume. Also, when the user has supplied volume data, the difference between the input volume and the calculated volume will be listed and an average calculated. The program will calculate the properties of either pure components or binary mixtures. For mixtures the mixing rules given by Huang (1986) and rewritten here as equations (5-22) through (5-24) are used.

The user must supply information in two files. The first contains the pure component and binary interaction (for mixtures only) parameters. The second contains PVT data with reference values. For the exact format required for these files, see the actual program listing.

PVT Data Regression

The second program listed here, PVTREG, will regress PVT data to the parameters in equation (5-19). The method used is that of maximum likelihood or generalized least squares. The method (Deming, 1943; Britt and Luecke, 1973; Anderson et al., 1978) accounts for random errors present in every data point. It assumes that the errors have a standard distribution about the "true" values with standard deviation supplied by the experimenter. The program varies the experimental values and equation parameters while meeting the constraints of the problem to obtain the most likely experimental values and the best parameters to describe them.

The calling routine, PVTREG, reads in data, selects the model and outputs the results. The main computations are done in the program GLSQ, written by H. I. Britt and R. H. Luecke at the DOE Morgantown Energy Technology Center and later incorporated into the ASPEN project at MIT. The routine GLSQ is completely general and can be used with any model. The user need only follow the format of the calling routine, PVTREG, and the model routine PVTSUB. The source code for GLSQ is on file with Dr. J. P. O'Connell in the Chemical Engineering Department at the University of Florida.

The user has the ability to pick from three models. For pure compounds, either the three parameters, C^*, V^* and T^* can be regressed or T^* can be supplied and only C^* and V^* regressed. For mixtures the pure components must be supplied and only the k_{12} is regressed. The PVT or PVTx data is supplied in a file also containing the reference pressures and volumes as well as standard deviations of each input variables. Any parameters required are supplied in a second file. For details of the input files see the listing of PVTREG.

Listing of Computer File PVTKT.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
c  program for solving liquid eos and kt equations of huang, o'connell
c
c  for eos must have reference point, rho0 at p0 and t and x (if binary)
c
c
c  input files
c
c  first file, contains parameters
c
c  line 1: description of data parameter source
c  line 2: c*[1]
c  line 3: v*[1], cc/gmole
c  line 4: t*[1], k
c  line 5: c*[2], only if binary
c  line 6: v*[2], cc/mole, only if binary
c  line 7: t*[2], k, only for binary
c  line 8: k12, only for binary, can equal zero
c
c  second file, contains pvt data (pure)
c
c  line 1: description of the pvt data
c  line 2: dummy line
c  line 3: p[bars], v[cc/gmole], t[k], pref, v[ref]
c  line n: continue with data in format of line 3
c
c  binary component data
c
c  line 1: description of the pvt data
c  line 2: dummy line
c  line 3: p[bars],v[cc/gmole],t[k],x,pref,v[ref]
c        . absolute standard deviations
c  line n: continue with data in format of line 3
c  any additional data on each line will be ignored, so that the input
c  files  do the data regression can be used here.
c
      implicit real*8(a-h,o-z)
      real*8 pres(250), tk(250), vol(250), pref(250), vref(250), x(250),
     >delv(250),kappat, kaptv
      character a, satfil*40, outfil*40, ans*1, descrp*80, mix*1,
     > dummy*80
1     continue
```

Listing of Computer File PVTKT.FOR

```
      write(*,'('' enter parameter data file name > '',\)')
      read(*,'(a)')satfil
      open (2,file=satfil)
      read(2,'(a)')descrp
      read(2,*)cstar,vstar,tstar
      write(*,'(''0are the calculations for a mixture[m] or a pure[p] co
     >mponent?, <p> '',\)')
      read(*,'(a)')mix
      if(mix .eq. 'm')read(2,*)cstar2,vstar2,tstar2,akij
      close (2)
      pref(1) = 0.0
      vref(1) = 0.0
c
c    use a file, containing up to 200 points, with a description on
c    line 1 and p,v,t,pref,vref on each following line, v = 0 if unknown
c    or p,v,t,x,pref,vref if binary mixture
c
2     write(*,'(''0enter data file name > '',\)')
      read(*,'(a)')satfil
      write(*,'(''0enter output file name > '',\)')
      read(*,'(a)')outfil
      open (3,file=satfil,status='old')
      open (4,file=outfil,status='new')
      write(4,1000)descrp,cstar,vstar,tstar
      read(3,'(a)')descrp
      read(3,'(a)')dummy
      do 100 i=1,200
         if(mix .eq. 'm') then
            read(3,*,end=200)pres(i),vol(i),tk(i),x(i),pref(i),vref(i)
         else
            read(3,*,end=200)pres(i),vol(i),tk(i),pref(i),vref(i)
         endif
100   continue
200   i = i - 1
      if(mix .eq. 'm')then
         write(4,1100)cstar2,vstar2,tstar2,akij
         if(vol(1) .eq. 0.0) then
            write(4,1300)descrp
         else
            write(4,1200)descrp
         endif
      else
         if(vol(1) .eq. 0.0) then
            write(4,1500)descrp
         else
            write(4,1400)descrp
         endif
```

Listing of Computer File PVTKT.FOR

```
      endif
      write(*,'(''0number of data points read: '',i5)')i
      num = i
      delsum = 0.0
      do 400 j=1,i
         denref = 1./vref(j)
         if(pref(j) .gt. pres(j)) then
            den = .999 * denref
         else
            den = 1.001 * denref
         endif
c
c  calculate the function and derivative
c
         if(mix .eq. 'm') then
            cmix = cstar*x(j) + cstar2*(1.0-x(j))
            tmix = tstar*x(j) + tstar2*(1.0-x(j))
            vmix = x(j)**2*vstar + (1.-x(j))**2*vstar2 +
     >         x(j)*(1.-x(j))*(vstar+vstar2)*(1.-akij)
         else
            cmix = cstar
            tmix = tstar
            vmix = vstar
         endif
         do 300 i = 1,1000
         dl = del(tk(j),pres(j),den,pref(j),denref,cmix,tmix,vmix)
            if(dabs(dl) .gt. .0001) then
               den = den - dl/vstar
            else
               goto 500
            endif
300      continue
         write(*,'('' too many itterations, den = '',g12.5)')den
         pause ' '
         goto 1
c
c  calculation of kappa t and print out
c
500      kappat = akt(den,tk(j),cmix,tmix,vmix)
         if(vol(j) .ne. 0.0) then
            denv = 1./vol(j)
            kaptv = akt(denv,tk(j),cmix,tmix,vmix)
         endif
         volc = 1. /den
         pkt1 = (1./kappat)*1.d4
         if(vol(j) .ne. 0.0) then
            delv(j) = vol(j) - volc
```

Listing of Computer File PVTKT.FOR

```
            delsum = delsum + dabs(delv(j))
            pkt2 = (1./kaptv)*1.d4
            if(mix .eq. 'm') then
               write(4,1600)pres(j),tk(j),vol(j),x(j),pkt2,volc,pkt1,
     >         pref(j),vref(j),delv(j)
            else
               write(4,1600)pres(j),tk(j),vol(j),pkt2,volc,pkt1,pref(j),
     >         vref(j),delv(j)
            endif
         else
            if(mix .eq. 'm') then
               write(4,1600)pres(j),tk(j),x(j),volc,pkt1,pref(j),vref(j)
            else
               write(4,1600)pres(j),tk(j),volc,pkt1,pref(j),vref(j)
            endif
         endif
400   continue
      delavg = delsum / num
      write(4,'(/,'' average absolute error (v) = '',g12.5)')delavg
      write(4,'(/,'' sum absolute error (v) = '',g12.5,i5)')delsum,num
      close(3)
      close(4)
      write(*,'(''0continue?, <n> '',\)')
      read(*,'(a)')ans
      if(ans .eq. 'y')goto 1
c
c  formats
c
1000  format(' source of parameters: ',a80,/,5x,' c1*: ',g12.5,
     >' v1*: ',g12.5,' t1*: ',g12.5,/)
1100  format(5x,' c2*: ',g12.5,' v2*: ',g12.5,' t2*: ',g12.5,' kij: ',
     >g12.5,/)
c binary vol entered
1200  format(' ',a80,/,/,
     >'   pressure  temperature    volume    mole fract     kappat     v
     >olume      kappat      pressure     volume      volume',/,
     >'   entered     entered     entered     entered     calculated  cal
     >culated  calculated     ref          ref          dif',/,
     >'     bar           k          cc/gmole  component 1   from pvt   fr
     >om eos     from eos      bar        cc/gmole     cc/gmole',/,
     >'                                                 (1/bar)x10^4  cc
     >/gmole  (1/bar)x10^4                  v(ent)-v(calc)',/,
     >' ================================================================
     >============================================================',/)
c pure vol entered
1400  format(' ',a80,/,/,
     >'   pressure  temperature    volume       kappat       volume      k
```

Listing of Computer File PVTKT.FOR

```
     >appat     pressure     volume     volume',/,
     >'   entered    entered    entered   calculated  calculated  cal
     >culated    ref         ref          dif',/,
     >'     bar         k         cc/gmole    from pvt    from eos    fr
     >om eos     bar       cc/gmole    cc/gmole',/,
     >'                                        (1/bar)x10^4  cc/gmole  (1/b
     >ar)x10^4                  v(ent)-v(calc)',/,
     >' ==================================================================
     >=================================================',/)
c binary no vol entered
1300 format(' ',a80,/,/,
     >'   pressure  temperature  mole fract    volume      kappat      pr
     >essure     volume',/,
     >'   entered    entered    entered   calculated  calculated
     >ref          ref',/,
     >'     bar         k       component 1   from eos    from eos
     >bar        cc/gmole',/,
     >'                                       cc/gmole  (1/bar)x10^4',/,
     >' ==================================================================
     >======================',/)
c pure no vol entered
1500 format(' ',a80,/,/,
     >'   pressure  temperature    volume       kappat      pressure     v
     >olume',/,
     >'   entered    entered    calculated  calculated     ref
     >ref',/,
     >'     bar         k        from eos     from eos       bar        cc
     >/gmole',/,
     >'                           cc/gmole  (1/bar)x10^4',/,
     >' ==================================================================
     >=========',/)
1600 format(' ',10g12.5)
     end
c
c----------------------------------------------------------------------
c  calculation of eos, f
c
      double precision function del(tk,pres,den,pref,denref,cstar,
     >tstar,vstar)
      implicit real*8(a-h,o-z)
      r = 83.1372
      rhor = den * vstar
      rhosr = denref * vstar
      tr = tk / tstar
      a = 9.8642 - 10.191/tr - 1.5356/(tr**2)
      b = - 14.2325 + 15.432/tr + 3.0147/(tr**2)
      c = 9.18067 - 10.966/tr - 2.90433/(tr**2)
```

Listing of Computer File PVTKT.FOR

```
      d = - 2.06515 + 3.18425/tr + 1.00425/(tr**2)
      f = pref -pres + (r/vstar)*tk*((rhor-rhosr) - cstar
     >  * (a * (rhor-rhosr) + b * (rhor**2 - rhosr**2)
     >  + c * (rhor**3 - rhosr**3) + d * (rhor**4 - rhosr**4)))
c
c  calculation of f'
c
      fp = (r/vstar)*tk*(1. - cstar * ( a
     >   + b * 2. * rhor + c * 3.* (rhor**2)
     >   + d * 4. * (rhor**3)))
c
c  calculation of f''
c
      fdp = (r/vstar)*tk*(-cstar*(2.*b + 6.*c*rhor + 16.*d*rhor**2))
c
      u = (f/fp)
      up = 1. - (f*fdp)/(fp**2)
      del = u/up
      end
c
c-----------------------------------------------------------------------
c  calculation of kt
c
      double precision function akt(den,tk,cstar,tstar,vstar)
      implicit real*8(a-h,o-z)
      r = 83.1372
      rhor = den * vstar
      tr = tk / tstar
      akt = den*r*tk*(1. - cstar*(9.8642 - 10.191/tr - 1.5356/(tr**2)
     >    - (28.465 - 30.864/tr - 6.0294/(tr**2)) * rhor + (27.542 -
     >       32.898/tr - 8.713/(tr**2))* rhor**2 - (8.2606 - 12.737/tr
     >    - 4.0170/(tr**2)) * rhor**3))
      end
```

Listing of Computer File PVTREG.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
c  parameter file, required for binary regression or to specify t*
c  line 1: c*[1]        line 1: t* (for regression of c*, v* for a pure)
c  line 2: v*[1], cc/gmole
c  line 3: t*[1], k
c  line 4: c*[2], only if binary
c  line 5: v*[2], cc/mole, only if binary
c  line 6: t*[2], k, only for binary
c
c  second file, contains pvt data and data errors
c
c  pure component data
c
c  line 1: description of the pvt data
c  line 2: # of data points
c  line 3: p[bars], v[cc/gmole], t[k], pref, v[ref], r(p), r(v), r(t)
c          absolute standard deviations
c  line n: continue with data in format of line 3
c
c  binary component data
c
c  line 1: description of the pvt data
c  line 2: # of data points
c  line 3: p[bars],v[cc/gmole],t[k],x,pref,v[ref],r(p),r(v),r(t),r(x)
c          absolute standard deviations
c  line n: continue with data in format of line 3
c$large
      implicit real*8(a-h,o-z)
      dimension param(7),var(28),obs(5,250),cor(5,250),err(5,250),
     >          sumerr(5),avgerr(5)
      external pvtmix,pvtpur,pvtkij, purcv
      character*1 ans, model*15, data*4, flnm*40, descrp*80, outfil*40,
     >          date*8, time*8
      character a
      write(*,'(''0do you wish to regress pure(p) or mixture(m) data?, <
     >p> '',\)')
      read(*,'(a)')ans
c
c  mixture regress kij only
c
      if(ans .eq. 'm') then
         call c1lp4v(obs,cor,err,param,var,descrp,flnm,pvtkij)
```

Listing of Computer File PVTREG.FOR

```
         n = 1
         iy = 4
      else
         write(*,'('' fit only c*, v*? <n> '',\)')
         read(*,'(a)')ans
         if(ans .eq. 'y') then
            call c12p3v(obs,cor,err,param,var,descrp,flnm,purcv)
            n = 2
            iy = 3
         else
            call c13p3v(obs,cor,err,param,var,descrp,flnm,pvtpur)
            n = 3
            iy = 3
         endif
      endif
      write(*,35)
35    format(/,/,20x,'pvt regression results huang & o''connell',/,
     >           21x,'parameters c*, v*, t*',10x,'errors',/)
      do 40 i = 1,n
         j = i*(i+1)/2
40    write(*,50)param(i),var(j)
50    format(' ',23x,f15.7,' +/- ',f15.7)
      pause ' '
      write(*,60)
60    format(' output residuals to a file, <n>? ',\)
      read(*,'(a)')ans
      if(ans .eq. 'y' .or. ans .eq. 'y') goto 65
      goto 999
65    write(*,'('' enter output file name > '',\)')
      read(*,'(a)')outfil
      open(2,file=outfil,status='new')
      if(n .eq. 1) write(2,36)descrp
      if(n .eq. 3) write(2,37)descrp
      if(n .eq. 2) write(2,39)descrp
      do 100 i = 1,n
         j = i*(i+1)/2
         sumerr(i) = 0.0
100   write(2,50)param(i),var(j)
      if(iy .eq. 3) then
         write(2,98)
      else
         write(2,97)
      endif
      do 80 i = 1,250
         if(obs(1,i) .eq. 0.0) goto 99
         if(iy .eq. 4) then
            write(2,90)(obs(j,i),cor(j,i),err(j,i),j=1,4)
```

```
          else
             write(2,95)(obs(j,i),cor(j,i),err(j,i),j=1,3)
          endif
          do 110 k = 1,iy
             sumerr(k) = sumerr(k) + dabs(err(k,i))
110       continue
80      continue
99      write(2,'(/)')
        do 120 k = 1,iy
           avgerr(k) = sumerr(k) / i
           write(2,'('' average absolute error variable '',i1,'' = '',
     >     g12.5,1x)')k,avgerr(k)
           write(*,'('' average absolute error variable '',i1,'' = '',
     >     g12.5,1x)')k,avgerr(k)
120     continue

36      format(/,/,a80,/,/,20x,
     >        'pvt regression results huang & o''connell',/,
     >         21x,'   parameter  kij    ',10x,'error',/)
37      format(/,/,a80,/,/,20x,
     >        'pvt regression results huang & o''connell',/,
     >        21x,'parameters c*, v*, t*',10x,'errors',/)
39      format(/,/,a80,/,/,20x,
     >        'pvt regression results huang & o''connell',/,
     >        19x,'parameters c1*, v1*,     ',9x,'errors',/)
90      format(12g11.5)
95      format(9g12.5)
97      format(' ',/, ' measured p estimate p  adjust p measured v estimat
     >e v  adjust v  measured t estimate t    adjust t measured x estima
     >te x  adjust x',/,/)
98      format(' ',/, ' measured p  estimate p    adjust p measured v  est
     >imate v     adjust v  measured t  estimate t     adjust t',/,/)
        close(2)
999     end
c
c-----------------------------------------------------------------------
c
      subroutine c13p3v(obs,cor,err,param,var,descrp,flnm,model)
c
c 3 parameters
c 1 constraint
c 3 variables + 2 non adjustable parameters for each point, refs
c
$large
      implicit real*8 (a-h,o-z)
      common /reals/ss,eps,ssnd,sumsq,sigma
      common /ints/nxn,ncxnc,ith,n,m,l,k,nc,iter,iterz,idem,iods,
     >             kout,ndriv,isv,nfeval,ier,ibound,nic,io
      external model
      character*40 flnm, descrp*80
c
c *******  note: dimension all variables to be equal to the     *******
c *******        values of n, l, nc, m, nxn, ncxnc as used      *******
c *******        by the current model.  make sure those         *******
c *******        arrays using k as a dimension are large        *******
c *******        enough for your data.                          *******
c
c *******        see below for information on structure of      *******
c *******        input data files.                              *******

c     dimensions:
c
c     k: # of expts.
c     n: # of parameters
c
c     integer mv(k), ncv(k), iwork(n)
      integer mv(250), ncv(250), iwork(3)
c
c     mv: number of variables for expt k
c     ncv: number of constraints on expt k
c     l: # of variables not to be adjusted
c     nc: max. # of constraints
c     m: max. # of variables
c     nxn = n(n+1)/2
c     ncxnc = nc(nc+1)/2
c
c     real*8 p(n),     zm(m,k),   x(l,k),      r(m,k),   const(10)
      real*8 p(3),param(3),zm(3,250),x(2,250),var(6),r(3,250),const(10)
c
c variables:
c     p(n):  parameters
c     zm(m,k): mth variable, kth experiment, as measured
c     x(l,k): lth variable, kth experiment, not to be adjusted
c     r(m,k): standard deviation of the mth variable, kth experiment
c     const(10): users definable constants, read in from a file
c
c     real*8 z(m,k),   f(nc,k),   delz(m,k),   covar(nxn), lb(n)
      real*8 z(3,250),   f(1,250),   delz(3,250),   covar(30),  lb(3)
c
c variables:
c     z(m,k): mth variable, kth experiment, adjusted
c     f(nc,k): ncth constraint, kth experiment
c     delz(m,k): difference between zm and z
c     lb(n): lower bound on p(n), not currently used
```

Listing of Computer File PVTREG.FOR

```
c
c     real*8 lm(n,n),  c(n,1),    d(1),        ub(n)
      real*8 lm(3,3),  c(3,1),    d(1),        ub(3)
c
c     variables
c     ub(n): upper bounds on parameters, not currently used
c
c     real*8 w(nc,nc,k),   zwork(m,k),  delp(n),      fprod(n)
      real*8 w(1,1,250),     zwork(3,250),  delp(3),      fprod(3)

c     real*8 fptwfp(nxn),  ft(nxn),     fptwfi(nxn),  ff(nc,k)
      real*8 fptwfp(6),    ft(6),       fptwfi(6),    ff(1,250)

c     real*8 fz(nc,m,k),   fp(nc,n,k),  fptw(n,nc,k), w1(ncxnc,k)
      real*8 fz(1,3,250),    fp(1,3,250),   fptw(3,1,250),  w1(1,250)

c     real*8 fzdz(nc,k),   scale(500)
      real*8 fzdz(1,250),    scale(500)

      real*8 obs(5,250), cor(5,250), err(5,250)
      n = 3
      nc = 1
      m = 3
      l = 2
c
c     ifixed = 0 no non-adjustable parameters
c     ifixed = 1 adjustable parameters
c
      ifixed = 1
c
c   icn = 1, user specified parameters in a separate file, i.e. const
c   icn = 0, no parameters
c
      icn = 0
      call genmain(icn,ifixed,mv,ncv,iwork,p,zm,x, r,const,
     >z,f,delz,covar,lb,lm,c,d,ub,w,zwork,
     >delp,fprod,fptwfp,ft,fptwfi,ff,fz,fp,fptw,w1,fzdz,scale,
     >descrp,flnm,model)
      do 1000 i = 1,n
1000  param(i) = p(i)
      nxn = n*(n+1)/2
      do 2000 i = 1,nxn
2000  var(i) = ft(i)
      do 3000 i = 1,m
         do 3000 j =1,k
            obs(i,j) = zm(i,j)
            cor(i,j) = z(i,j)
```

Listing of Computer File PVTREG.FOR

```
            err(i,j) = delz(i,j)
3000    continue
        pause ' '
        nxn = n*(n+1)/2
        do 30 i = 1,nxn
           var(i) = (dabs(var(i)))**(1./2.)
30      continue
        end
c
c-------------------------------------------------------------------
c
        subroutine c1lp4v(obs,cor,err,param,var,descrp,flnm,model)
c
c 1 parameters
c 1 constraint
c 4 variables + 2 non adjustable parameters for each point, refs
c
$large
        implicit real*8 (a-h,o-z)
        common /reals/ss,eps,ssnd,sumsq,sigma
        common /ints/nxn,ncxnc,ith,n,m,l,k,nc,iter,iterz,idem,iods,
     >             kout,ndriv,isv,nfeval,ier,ibound,nic,io
        external model
        character*40 flnm, descrp*80
        integer mv(250), ncv(250), iwork(1)
        real*8 p(1),param(1),zm(4,250),x(2,250),var(1),r(4,250),const(10)
        real*8 z(4,250),   f(1,250),    delz(4,250),    covar(30),   lb(1)
        real*8 lm(1,1),  c(1,1),    d(1),         ub(1)
        real*8 w(1,1,250),     zwork(4,250),  delp(1),       fprod(1)
        real*8 fptwfp(1),     ft(1),         fptwfi(1),     ff(1,250)
        real*8 fz(1,4,250),    fp(1,1,250),   fptw(1,1,250),  w1(1,250)
        real*8 fzdz(1,250),    scale(500)
        real*8 obs(5,250), cor(5,250), err(5,250)
        n = 1
        nc = 1
        m = 4
        l =.2
        ifixed = 1
        icn = 1
        call genmain(icn,ifixed,mv,ncv,iwork,p,zm,x, r,const,
     >z,f,delz,covar,lb,lm,c,d,ub,w,zwork,
     >delp,fprod,fptwfp,ft,fptwfi,ff,fz,fp,fptw,w1,fzdz,scale,
     >descrp,flnm,model)
        do 1000 i = 1,n
1000    param(i) = p(i)
        nxn = n*(n+1)/2
        do 2000 i = 1,nxn
```

Listing of Computer File PVTREG.FOR

```
2000  var(i) = ft(i)
      do 3000 i = 1,m
         do 3000 j =1,k
            obs(i,j) = zm(i,j)
            cor(i,j) = z(i,j)
            err(i,j) = delz(i,j)
3000  continue
      pause ' '
      nxn = n*(n+1)/2
      do 30 i = 1,nxn
         var(i) = (dabs(var(i)))**(1./2.)
30    continue
      end
c
      subroutine c12p3v(obs,cor,err,param,var,descrp,flnm,model)
c
c 2 parameters
c 1 constraint
c 3 variables + 2 non adjustable parameters for each point, refs
c
$large
      implicit real*8 (a-h,o-z)
      common /reals/ss,eps,ssnd,sumsq,sigma
      common /ints/nxn,ncxnc,ith,n,m,l,k,nc,iter,iterz,idem,iods,
     >             kout,ndriv,isv,nfeval,ier,ibound,nic,io
      external model
      character*40 flnm, descrp*80
      integer mv(250), ncv(250), iwork(2)
      real*8 p(2),param(2),zm(3,250),x(2,250),var(6),r(3,250),const(10)
      real*8 z(3,250),   f(1,250),    delz(3,250),   covar(30),  lb(2)
      real*8 lm(2,2),  c(2,1),   d(1),        ub(2)
      real*8 w(1,1,250),     zwork(3,250),  delp(2),      fprod(2)
      real*8 fptwfp(3),    ft(3),        fptwfi(3),    ff(1,250)
      real*8 fz(1,3,250),    fp(1,2,250),   fptw(2,1,250),  w1(1,250)
      real*8 fzdz(1,250),    scale(500)
      real*8 obs(5,250), cor(5,250), err(5,250)
      n = 2
      nc = 1
      m = 3
      l = 2
      ifixed = 1
      icn = 1
      call genmain(icn,ifixed,mv,ncv,iwork,p,zm,x, r,const,
     >z,f,delz,covar,lb,lm,c,d,ub,w,zwork,
     >delp,fprod,fptwfp,ft,fptwfi,ff,fz,fp,fptw,w1,fzdz,scale,
     >descrp,flnm,model)
      do 1000 i = 1,n
```

Listing of Computer File PVTREG.FOR

```
1000   param(i) = p(i)
       nxn = n*(n+1)/2
       do 2000 i = 1,nxn
2000   var(i) = ft(i)
       do 3000 i = 1,m
          do 3000 j =1,k
             obs(i,j) = zm(i,j)
             cor(i,j) = z(i,j)
             err(i,j) = delz(i,j)
3000   continue
       pause ' '
       nxn = n*(n+1)/2
       do 30 i = 1,nxn
          var(i) = (dabs(var(i)))**(1./2.)
30     continue
       end
```

Listing of Computer File PVTSUB.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
c
c  liquid pvt equation huang & o'connell  pure components
c  1 constraint, 3 parameters, 2 variables, 2 non-adjustable params
c
      subroutine pvtpur(z,zm,x,p,k,q,qv,l,n,m,mv,key,f,fz,fp,const)
      implicit real*8(a-h,o-z)
      integer q,qv(k),mv(k)
      real*8 z(q,k), zm(q,k), p(n), f(m,k), fz(m,q,k), fp(m,n,k),
     >       x(l,k), const(10)
      do 10 i = 1,k
c
c  constraint function
c  x(1,k); reference pressure @ t [z(3,i)]
c  x(2,k); reference volume @ t [z(3,i)]
c  z(1,k); pressure, bars
c  z(2,k); volume, cc/gmole
c  z(3,k); temperature, k
c  p(1);    c*
c  p(2);    v*
c  p(3);    t*
c  r:       gas constant
c
         r = 83.1372
         rhor   = p(2) / z(2,i)
         tr     = z(3,i) / p(3)
         rhoref = p(2) / x(2,i)
         a =   9.8642   - 10.191   / tr - 1.5356   / tr**2
         b = -14.2325   + 15.432   / tr + 3.0147   / tr**2
         c =   9.18067  - 10.966   / tr - 2.90433  / tr**2
         d = - 2.06515  + 3.18425  / tr + 1.00425  / tr**2
         f(1,i) = x(1,i) - z(1,i) + r*z(3,i)/p(2) *
     >            ((rhor - rhoref) - p(1)*( a * (rhor - rhoref) +
     >            b * (rhor**2 - rhoref**2) + c * (rhor**3 -
     >            rhoref**3) + d * (rhor**4 - rhoref**4)))
c
10    continue
      end
c
c---------------------------------------------------------------------
c
c  liquid pvt equation huang & o'connell
```

Listing of Computer File PVTSUB.FOR

```
c  fit kij only
c  1 constraint, 1 adjustable variable, 2 fixed variables, 6 constants
c
      subroutine pvtkij(z,zm,x,p,k,q,qv,l,n,m,mv,key,f,fz,fp,const)
      implicit real*8(a-h,o-z)
      integer q,qv(k),mv(k)
      real*8 z(q,k), zm(q,k), p(n), f(m,k), fz(m,q,k), fp(m,n,k),
     >      x(l,k), const(10)
      do 10 i = 1,k
c
c  constraint function
c  x(1,k); reference pressure @ t [z(3,i)] and x [z(4,i)]
c  x(2,k); reference volume @ t [z(3,i)] and x [z(4,i)]
c  z(1,k); pressure, bars
c  z(2,k); volume, cc/gmole
c  z(3,k); temperature, k
c  z(4,k); mole fraction, component 1
c  const(1); c1*
c  const(2); v1*
c  const(3); t1*
c  const(4); c2*
c  const(5); v2*
c  const(6); t2*
c  p(1);    kij
c  r:       gas constant
c
        if(z(4,i) .lt. 0.0) z(4,i) = 0.0
        if(z(4,1) .gt. 1.0) z(4,i) = 1.0
        r = 83.1372
        cmix = z(4,i)*const(1) + (1.-z(4,i))*const(4)
        tmix = z(4,i)*const(3) + (1.-z(4,i))*const(6)
        vmix = z(4,i)**2*const(2) + z(4,i)*(1.-z(4,i))
     >      * (const(2)+const(5)) * (1.-p(1)) + (1.-z(4,i))**2*const(5)

        rhor   = vmix / z(2,i)
        tr     = z(3,i) / tmix
        rhoref = vmix / x(2,i)
        a =   9.8642  - 10.191  / tr - 1.5356  / tr**2
        b = -14.2325  + 15.432  / tr + 3.0147  / tr**2
        c =   9.18067 - 10.966  / tr - 2.90433 / tr**2
        d = - 2.06515 + 3.18425 / tr + 1.00425 / tr**2
        f(1,i) = x(1,i) - z(1,i) + r*z(3,i)/vmix *
     >          ((rhor - rhoref) - cmix*( a * (rhor - rhoref) +
     >          b * (rhor**2 - rhoref**2) + c * (rhor**3 -
     >          rhoref**3) + d * (rhor**4 - rhoref**4)))
c
10    continue
```

Listing of Computer File PVTSUB.FOR

```
      end
c-----------------------------------------------------------------------
c
c  liquid pvt equation huang & o'connell  pure components
c  1 constraint, 2 parameters, 2 variables, 2 non-adjustable params
c
      subroutine purcv(z,zm,x,p,k,q,qv,l,n,m,mv,key,f,fz,fp,const)
      implicit real*8(a-h,o-z)
      integer q,qv(k),mv(k)
      real*8 z(q,k), zm(q,k), p(n), f(m,k), fz(m,q,k), fp(m,n,k),
     >       x(l,k), const(10)
      do 10 i = 1,k
c
c  constraint function
c  x(1,k); reference pressure @ t [z(3,i)]
c  x(2,k); reference volume @ t [z(3,i)]
c  z(1,k); pressure, bars
c  z(2,k); volume, cc/gmole
c  z(3,k); temperature, k
c  p(1);   c*
c  p(2);   v*
c  const(1); t*
c  r:      gas constant
c
         r = 83.1372
         rhor   = p(2) / z(2,i)
         tr     = z(3,i) / const(1)
         rhoref = p(2) / x(2,i)
         a =   9.8642  - 10.191  / tr - 1.5356  / tr**2
         b = -14.2325  + 15.432  / tr + 3.0147  / tr**2
         c =   9.18067 - 10.966  / tr - 2.90433 / tr**2
         d = - 2.06515 + 3.18425 / tr + 1.00425 / tr**2
         f(1,i) = x(1,i) - z(1,i) + r*z(3,i)/p(2) *
     >            ((rhor - rhoref) - p(1)*( a * (rhor - rhoref) +
     >            b * (rhor**2 - rhoref**2) + c * (rhor**3 -
     >            rhoref**3) + d * (rhor**4 - rhoref**4)))
c
10    continue
      end
```

APPENDIX H
DIRECT CORRELATION FUNCTION INTEGRAL DATABASE

The database of calculated direct correlation function integrals (DCFI) are given as a function of mole fraction at constant temperature and at low pressure (one bar). All the data necessary to to calculate the DCFIs are given in the tables. Further, various equation parameters required for calculation of the fundamental inputs, such as volume, partial molar volume, isothermal compressibility and activity coefficient derivatives are either given in these tables or in Chapter 5. References and further explanations of the input data are also given in Chapter 5.

The pure component volumes in the tables are all taken from DIPPR (Daubert and Danner, 1985). Sources for excess volume data can be found in Table 5-1, the actual parameters used are listed here. Using these parameters and the equations in Appendix D the mixture volume (V) and partial molar volumes ($\overline{V}_1$, $\overline{V}_2$) can be calculated. Equations (5-21) - (5-24) are used calculation of isothermal compressibility of all systems except chloroform/diethyl ether, carbon disulfide/acetone, dichloroethane/benzene, cyclopentane/cyclooctane, cyclopentane/OMCTS, chlorobenzene/aniline, nitrobenzene/aniline and benzene/aniline. Parameters and references for these equations are given in Tables 5-3 and 5-4. For systems not found in Table 5-4 and not exempted above, the binary parameter is zero. For the systems exempted above, see the text of Chapter 5 for an explanation.

References for the activity coefficient parameters given in these tables can be found in Table 5-2. The parameters given here are the λ_{ij} values for the Wilson model are for the following equations describing a binary

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad \text{(H-1}$$

$$\ln\gamma_2 = -\ln(x_1 + \Lambda_{12}x_2) - x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad \text{(H-2}$$

$$\left(\frac{\partial\ln\gamma_1}{\partial x_1}\right) = -\frac{1}{x_1 + \Lambda_{12}x_2} + \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} + \frac{x_2\Lambda_{12}(\Lambda_{12} - 1)}{(x_1 + \Lambda_{12}x_2)^2} + \frac{x_2\Lambda_{21}(\Lambda_{21} - 1)}{(x_2 + \Lambda_{21}x_1)^2} \qquad \text{(H-3}$$

$$\left(\frac{\partial\ln\gamma_2}{\partial x_2}\right) = -\frac{1}{x_2 + \Lambda_{21}x_1} + \frac{\Lambda_{12}}{\Lambda_{12}x_2 + x_1} + \frac{x_1\Lambda_{21}(\Lambda_{21} - 1)}{(x_2 + \Lambda_{21}x_1)^2} + \frac{x_1\Lambda_{12}(\Lambda_{12} - 1)}{(x_1 + \Lambda_{12}x_2)^2} \qquad \text{(H-4}$$

where $\Lambda_{12} = \frac{V_2^o}{V_1^o} \exp -\frac{\lambda_{12}}{RT}$, $\Lambda_{21} = \frac{V_1^o}{V_2^o} \exp -\frac{\lambda_{21}}{RT}$

and R = 1.987 cal/gmol K.

for NRTL, values of the g_{ij} parameters are given for

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \left(\frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right)\right] \qquad \text{(H-5}$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \left(\frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right)\right] \qquad \text{(H-6}$$

$$\left(\frac{\partial\ln\gamma_1}{\partial x_1}\right) = \frac{2\tau_{21}G_{21}^2x_2}{(x_1 + x_2G_{21})^2} + \frac{2\tau_{12}G_{12}x_2}{(x_2 + x_1G_{12})^2}$$

$$+ \frac{2\tau_{12}(G_{12}-G_{12}^2)x_2^2}{(x_2 + x_1G_{12})^3} + \frac{2\tau_{21}(G_{21}^3-G_{21}^2)x_2^2}{(x_1 + x_2G_{21})^3} \qquad \text{(H-7}$$

$$\left(\frac{\partial\ln\gamma_2}{\partial x_2}\right) = \frac{2\tau_{12}G_{12}^2x_1}{(x_2 + x_1G_{12})^2} + \frac{2\tau_{21}G_{21}x_1}{(x_1 + x_2G_{21})^2}$$

$$+ \frac{2\tau_{21}(G_{21}-G_{21}^2)x_1^2}{(x_1 + x_2G_{21})^3} + \frac{2\tau_{12}(G_{12}^3-G_{12}^2)x_1^2}{(x_2 + x_1G_{12})^3} \qquad \text{(H-8}$$

where

$$\tau_{12} = \frac{g_{12}}{RT},\ \tau_{21} = \frac{g_{21}}{RT},\ G_{12} = \exp(-\alpha\,\tau_{12}),\ G_{21} = \exp(-\alpha\,\tau_{21})$$

and R = 1.987 cal/gmole K

Also listed in these tables are composition ρ_1 and ρ_2 which are calculated by

$$\rho_1 = x_1 / V \tag{H-9}$$

$$\rho_2 = x_2 / V \tag{H-10}$$

The bulk modulus (χ), given in these tables, can be calculated from the isothermal compressibility κ_T,

$$\chi = 1 / \rho \kappa_T RT \tag{H-11}$$

where ρ is the density, ρ_1+ρ_2, and R is the gas constant.

The DCFIs given in these tables (C_{11} , C_{12} , C_{22}) can be calculated using equations 5-6 through 5-8. The ideal DCFIs (C_{11}^{ID} , C_{12}^{ID} , C_{22}^{ID}) are calculated using equations 5-9 through 5-11. The quantities ΔC and 1/ΔC are given by the following expression

$$\Delta C = [(1 - C_{11})(1 - C_{22}) - (1 - C_{12})^2] \tag{H-12}$$

Table H-1
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Methanol(2)
T: 20° C

Pure Component Volumes

V_1^o : 96.5922

V_2^o : 40.4699

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.1562

υ_1 : -0.2330

υ_2 : 0.1285

υ_3 : -0.2007

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 172.1181

λ_{21} : 2561.4177

NRTL, Eq. H-7,8

g_{12} : 1749.46

g_{21} : 941.2561

α : .4957

This Study, Eq. 5-39

a : -0.02043

b : 0.01992

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	73.396	33.178	13.967	79.568	33.337	13.967	-75.616	-1.322
0.05	71.122	31.958	13.325	75.361	31.574	13.229	-73.606	-1.359
0.10	68.642	30.712	12.684	71.576	29.989	12.565	-72.539	-1.379
0.15	66.109	29.486	12.058	68.153	28.555	11.964	-72.276	-1.384
0.20	63.612	28.308	11.454	65.043	27.251	11.418	-72.741	-1.375
0.25	61.199	27.189	10.872	62.204	26.062	10.919	-73.906	-1.353
0.30	58.897	26.134	10.310	59.603	24.972	10.463	-75.781	-1.320
0.35	56.716	25.143	9.764	57.210	23.970	10.043	-78.417	-1.275
0.40	54.656	24.212	9.228	55.002	23.045	9.655	-81.908	-1.221
0.45	52.713	23.339	8.694	52.959	22.188	9.296	-86.407	-1.157
0.50	50.882	22.518	8.155	51.061	21.393	8.963	-92.144	-1.085
0.55	49.154	21.746	7.597	49.295	20.654	8.653	-99.467	-1.005
0.60	47.523	21.020	7.006	47.647	19.963	8.364	-108.91	-0.918
0.65	45.983	20.338	6.357	46.106	19.317	8.093	-121.32	-0.824
0.70	44.529	19.699	5.613	44.661	18.712	7.840	-138.10	-0.724
0.75	43.159	19.102	4.706	43.304	18.143	7.602	-161.77	-0.618
0.80	41.871	18.549	3.506	42.027	17.608	7.377	-197.25	-0.507
0.85	40.667	18.039	1.717	40.823	17.104	7.166	-255.59	-0.391
0.90	39.550	17.568	-1.489	39.687	16.628	6.967	-367.54	-0.272
0.95	38.526	17.094	-9.501	38.611	16.177	6.778	-658.25	-0.152
1.00	37.593	15.909	-60.243	37.593	15.751	6.599	-2517.8	-0.040

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-1 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	24.710	13.967	-5.414	0.000	-7.506	0.000	96.131	40.470
0.05	1.156	21.962	15.240	-4.588	-0.241	-6.047	-0.318	96.268	40.467
0.10	2.172	19.544	16.489	-3.959	-0.440	-4.929	-0.548	96.365	40.459
0.15	3.071	17.401	17.718	-3.467	-0.612	-4.062	-0.717	96.433	40.449
0.20	3.872	15.490	18.933	-3.074	-0.768	-3.386	-0.847	96.480	40.439
0.25	4.591	13.774	20.136	-2.753	-0.918	-2.856	-0.952	96.514	40.429
0.30	5.240	12.226	21.329	-2.487	-1.066	-2.440	-1.046	96.540	40.420
0.35	5.827	10.822	22.513	-2.264	-1.219	-2.114	-1.139	96.561	40.409
0.40	6.362	9.543	23.689	-2.075	-1.383	-1.861	-1.241	96.580	40.398
0.45	6.851	8.374	24.857	-1.912	-1.564	-1.666	-1.363	96.596	40.386
0.50	7.300	7.300	26.018	-1.771	-1.771	-1.521	-1.521	96.611	40.373
0.55	7.713	6.311	27.172	-1.647	-2.013	-1.416	-1.731	96.625	40.358
0.60	8.095	5.397	28.319	-1.538	-2.307	-1.347	-2.021	96.635	40.344
0.65	8.449	4.549	29.460	-1.441	-2.677	-1.307	-2.428	96.642	40.333
0.70	8.778	3.762	30.598	-1.354	-3.159	-1.291	-3.013	96.644	40.328
0.75	9.084	3.028	31.734	-1.274	-3.823	-1.292	-3.875	96.641	40.336
0.80	9.370	2.342	32.873	-1.200	-4.800	-1.295	-5.180	96.634	40.362
0.85	9.638	1.701	34.020	-1.127	-6.386	-1.275	-7.227	96.622	40.417
0.90	9.890	1.099	35.183	-1.045	-9.402	-1.176	-10.58	96.609	40.511
0.95	10.128	0.533	36.370	-0.905	-17.19	-0.863	-16.40	96.597	40.658
1.00	10.353	-0.000	37.593	0.000	-66.98	0.000	-27.27	96.592	40.876

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-2
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Acetonitrile(2)
T: 45° C

Pure Component Volumes

V_1^o : 99.4845

V_2^o : 54.1655

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.3668

υ_1 : 0.05676

υ_2 : 0.3072

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : 191.6619	g_{12} : 1090.251
λ_{21} : 1510.4098	g_{21} : 669.0096
	α : 0.5185

This Study, Eq. 5-39

a : -0.02169

b : 0.01760

x_1	$(1\text{-}C_{11})$	$(1\text{-}C_{12})$	$(1\text{-}C_{22})$	$(1\text{-}C_{11})^{ID}$	$(1\text{-}C_{12})^{ID}$	$(1\text{-}C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	50.781	29.798	16.224	54.731	29.799	16.224	-64.020	-1.562
0.05	52.110	30.398	16.466	52.479	28.573	15.557	-66.022	-1.515
0.10	52.888	30.714	16.551	50.404	27.443	14.942	-68.031	-1.470
0.15	53.202	30.787	16.498	48.488	26.400	14.374	-70.095	-1.427
0.20	53.122	30.651	16.325	46.712	25.433	13.847	-72.262	-1.384
0.25	52.707	30.335	16.044	45.062	24.534	13.358	-74.578	-1.341
0.30	52.004	29.865	15.669	43.524	23.697	12.902	-77.097	-1.297
0.35	51.056	29.263	15.208	42.088	22.915	12.476	-79.880	-1.252
0.40	49.901	28.550	14.671	40.743	22.183	12.078	-83.002	-1.205
0.45	48.572	27.743	14.064	39.482	21.496	11.704	-86.561	-1.155
0.50	47.099	26.860	13.393	38.296	20.851	11.352	-90.681	-1.103
0.55	45.509	25.916	12.660	37.180	20.243	11.022	-95.530	-1.047
0.60	43.830	24.926	11.863	36.127	19.670	10.709	-101.34	-0.987
0.65	42.082	23.900	10.998	35.131	19.128	10.414	-108.42	-0.922
0.70	40.288	22.850	10.049	34.190	18.615	10.135	-117.27	-0.853
0.75	38.467	21.784	8.994	33.297	18.129	9.871	-128.59	-0.778
0.80	36.636	20.705	7.785	32.450	17.668	9.619	-143.52	-0.697
0.85	34.809	19.614	6.341	31.645	17.229	9.381	-163.99	-0.610
0.90	32.999	18.498	4.506	30.879	16.812	9.154	-193.46	-0.517
0.95	31.214	17.324	1.964	30.149	16.415	8.937	-238.80	-0.419
1.00	29.452	16.001	-2.020	29.452	16.036	8.731	-315.54	-0.317

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-2 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	18.462	16.224	-3.946	0.000	-4.241	0.000	99.482	54.166
0.05	0.886	16.836	17.879	-3.508	-0.185	-3.725	-0.196	99.369	54.168
0.10	1.704	15.336	19.464	-3.146	-0.350	-3.292	-0.366	99.295	54.174
0.15	2.461	13.948	20.968	-2.842	-0.501	-2.927	-0.517	99.251	54.180
0.20	3.165	12.659	22.381	-2.583	-0.646	-2.619	-0.655	99.233	54.184
0.25	3.820	11.460	23.695	-2.361	-0.787	-2.360	-0.787	99.235	54.183
0.30	4.431	10.340	24.901	-2.167	-0.929	-2.140	-0.917	99.251	54.177
0.35	5.003	9.292	25.994	-1.997	-1.076	-1.954	-1.052	99.277	54.164
0.40	5.539	8.309	26.969	-1.847	-1.231	-1.796	-1.197	99.309	54.145
0.45	6.043	7.385	27.823	-1.711	-1.400	-1.661	-1.359	99.344	54.119
0.50	6.516	6.516	28.553	-1.588	-1.588	-1.544	-1.544	99.379	54.088
0.55	6.962	5.696	29.159	-1.474	-1.802	-1.442	-1.763	99.411	54.052
0.60	7.383	4.922	29.641	-1.368	-2.051	-1.351	-2.026	99.439	54.015
0.65	7.781	4.190	30.002	-1.265	-2.349	-1.264	-2.347	99.461	53.977
0.70	8.157	3.496	30.243	-1.163	-2.714	-1.177	-2.746	99.478	53.943
0.75	8.514	2.838	30.369	-1.059	-3.176	-1.083	-3.248	99.488	53.916
0.80	8.852	2.213	30.384	-0.945	-3.779	-0.972	-3.886	99.493	53.900
0.85	9.174	1.619	30.294	-0.812	-4.601	-0.831	-4.710	99.493	53.900
0.90	9.480	1.053	30.104	-0.643	-5.784	-0.643	-5.787	99.490	53.920
0.95	9.773	0.514	29.821	-0.400	-7.607	-0.380	-7.215	99.486	53.968
1.00	10.052	-0.000	29.452	0.000	-10.71	0.000	-9.141	99.485	54.049

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-3
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Ethanol(2)
T: 20° C

Pure Component Volumes

V_1^o : 96.5922

V_2^o : 58.1745

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.26724

υ_1 : -0.82323

υ_2 : -0.14107

υ_3 : -0.42321

υ_4 : 0.56169

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 124.8773

λ_{21} : 2296.2184

NRTL, Eq. H-7,8

g_{12} : 1666.2903

g_{21} : 577.1476

α : 0.4883

This Study, Eq. 5-39

a : -0.02032

b : 0.01978

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	57.533	36.944	22.505	62.043	37.366	22.505	-70.074	-1.427
0.05	56.816	36.338	21.999	60.089	36.190	21.796	-70.568	-1.417
0.10	56.022	35.676	21.445	58.254	35.085	21.130	-71.371	-1.401
0.15	55.103	34.943	20.844	56.528	34.045	20.504	-72.482	-1.380
0.20	54.054	34.149	20.206	54.901	33.065	19.914	-73.935	-1.353
0.25	52.896	33.311	19.545	53.366	32.140	19.357	-75.787	-1.319
0.30	51.661	32.453	18.874	51.914	31.266	18.830	-78.119	-1.280
0.35	50.388	31.595	18.202	50.538	30.438	18.332	-81.041	-1.234
0.40	49.108	30.754	17.535	49.234	29.652	17.859	-84.693	-1.181
0.45	47.849	29.941	16.870	47.996	28.906	17.409	-89.262	-1.120
0.50	46.628	29.165	16.204	46.818	28.197	16.982	-95.002	-1.053
0.55	45.457	28.425	15.524	45.696	27.522	16.575	-102.28	-0.978
0.60	44.339	27.721	14.814	44.628	26.878	16.188	-111.62	-0.896
0.65	43.273	27.052	14.049	43.607	26.263	15.818	-123.88	-0.807
0.70	42.256	26.417	13.192	42.633	25.677	15.464	-140.43	-0.712
0.75	41.286	25.819	12.180	41.701	25.115	15.126	-163.73	-0.611
0.80	40.367	25.267	10.895	40.809	24.578	14.803	-198.62	-0.503
0.85	39.509	24.777	9.062	39.955	24.063	14.493	-255.88	-0.391
0.90	38.733	24.371	5.905	39.135	23.570	14.195	-365.20	-0.274
0.95	38.079	24.046	-1.749	38.348	23.096	13.910	-644.78	-0.155
1.00	37.593	23.186	-46.528	37.593	22.641	13.636	-2286.7	-0.044

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-3 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	17.190	22.505	-3.114	0.000	-3.565	0.000	95.499	58.175
0.05	0.833	15.821	23.448	-2.859	-0.150	-3.159	-0.166	95.676	58.170
0.10	1.615	14.533	24.352	-2.638	-0.293	-2.812	-0.312	95.895	58.152
0.15	2.350	13.319	25.210	-2.444	-0.431	-2.517	-0.444	96.114	58.120
0.20	3.043	12.172	26.022	-2.273	-0.568	-2.266	-0.566	96.307	58.080
0.25	3.696	11.088	26.792	-2.122	-0.707	-2.053	-0.684	96.462	58.035
0.30	4.312	10.062	27.528	-1.986	-0.851	-1.875	-0.803	96.575	57.992
0.35	4.895	9.091	28.239	-1.865	-1.004	-1.726	-0.930	96.651	57.956
0.40	5.447	8.170	28.931	-1.756	-1.171	-1.605	-1.070	96.697	57.929
0.45	5.970	7.297	29.614	-1.658	-1.356	-1.509	-1.235	96.721	57.911
0.50	6.467	6.467	30.290	-1.568	-1.568	-1.435	-1.435	96.731	57.902
0.55	6.939	5.678	30.965	-1.486	-1.817	-1.381	-1.688	96.735	57.898
0.60	7.389	4.926	31.639	-1.411	-2.117	-1.345	-2.018	96.736	57.896
0.65	7.818	4.210	32.313	-1.342	-2.492	-1.326	-2.462	96.736	57.897
0.70	8.227	3.526	32.988	-1.277	-2.980	-1.317	-3.074	96.733	57.903
0.75	8.618	2.873	33.667	-1.216	-3.648	-1.314	-3.943	96.725	57.925
0.80	8.992	2.248	34.356	-1.156	-4.625	-1.303	-5.211	96.708	57.984
0.85	9.351	1.650	35.067	-1.095	-6.202	-1.258	-7.129	96.681	58.113
0.90	9.696	1.077	35.820	-1.020	-9.176	-1.127	-10.14	96.646	58.365
0.95	10.030	0.528	36.646	-0.880	-16.72	-0.796	-15.13	96.610	58.818
1.00	10.353	-0.000	37.593	0.000	-60.83	0.000	-23.88	96.592	59.574

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-4
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Acetone(2)
T: 45° C

Pure Component Volumes

V_1^o : 99.4845

V_2^o : 76.2355

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.22944

υ_1 : -0.46748

υ_2 : 0.18718

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -104.2622

λ_{21} : 770.8949

NRTL, Eq. H-7,8

g_{12} : 703.7136

g_{21} : -56.2495

α : 0.2985

This Study, Eq. 5-39

a : -0.04406

b : 0.03505

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	31.342	24.961	19.226	32.741	25.090	19.226	-20.466	-4.886
0.05	32.740	26.014	19.979	32.559	24.950	19.120	-22.592	-4.426
0.10	33.905	26.883	20.584	32.379	24.812	19.014	-24.767	-4.038
0.15	34.847	27.576	21.047	32.202	24.676	18.910	-26.993	-3.705
0.20	35.577	28.103	21.376	32.026	24.541	18.806	-29.278	-3.416
0.25	36.105	28.473	21.578	31.852	24.408	18.704	-31.631	-3.161
0.30	36.446	28.697	21.661	31.680	24.276	18.603	-34.062	-2.936
0.35	36.612	28.786	21.633	31.510	24.146	18.503	-36.587	-2.733
0.40	36.617	28.752	21.504	31.341	24.017	18.404	-39.224	-2.549
0.45	36.477	28.606	21.282	31.175	23.889	18.306	-41.997	-2.381
0.50	36.207	28.362	20.975	31.010	23.763	18.210	-44.933	-2.226
0.55	35.821	28.029	20.590	30.847	23.638	18.114	-48.071	-2.080
0.60	35.335	27.621	20.135	30.685	23.514	18.019	-51.455	-1.943
0.65	34.764	27.148	19.614	30.525	23.392	17.925	-55.143	-1.813
0.70	34.121	26.620	19.033	30.367	23.271	17.832	-59.206	-1.689
0.75	33.420	26.046	18.391	30.211	23.151	17.741	-63.738	-1.569
0.80	32.674	25.433	17.690	30.056	23.032	17.650	-68.859	-1.452
0.85	31.894	24.790	16.925	29.903	22.915	17.560	-74.725	-1.338
0.90	31.092	24.118	16.086	29.751	22.798	17.471	-81.546	-1.226
0.95	30.276	23.421	15.159	29.601	22.683	17.382	-89.607	-1.116
1.00	29.452	22.695	14.117	29.452	22.569	17.295	-99.305	-1.007

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-4 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	13.117	19.226	-1.065	0.000	-0.972	-0.000	98.975	76.236
0.05	0.646	12.278	20.584	-1.043	-0.055	-0.970	-0.051	99.046	76.234
0.10	1.274	11.463	21.851	-1.020	-0.113	-0.966	-0.107	99.120	76.228
0.15	1.883	10.670	23.023	-0.997	-0.176	-0.960	-0.169	99.193	76.217
0.20	2.475	9.899	24.097	-0.972	-0.243	-0.950	-0.238	99.263	76.202
0.25	3.050	9.150	25.071	-0.946	-0.315	-0.938	-0.313	99.329	76.183
0.30	3.609	8.421	25.946	-0.919	-0.394	-0.922	-0.395	99.389	76.161
0.35	4.152	7.711	26.723	-0.890	-0.479	-0.902	-0.486	99.440	76.136
0.40	4.681	7.021	27.401	-0.859	-0.573	-0.878	-0.585	99.484	76.110
0.45	5.195	6.349	27.985	-0.825	-0.675	-0.849	-0.695	99.519	76.084
0.50	5.695	5.695	28.476	-0.789	-0.789	-0.815	-0.815	99.544	76.061
0.55	6.181	5.057	28.880	-0.749	-0.915	-0.774	-0.946	99.560	76.043
0.60	6.655	4.437	29.200	-0.705	-1.057	-0.728	-1.091	99.568	76.033
0.65	7.117	3.832	29.443	-0.656	-1.217	-0.673	-1.251	99.568	76.033
0.70	7.567	3.243	29.612	-0.600	-1.400	-0.611	-1.426	99.561	76.048
0.75	8.006	2.669	29.715	-0.536	-1.609	-0.539	-1.618	99.549	76.080
0.80	8.434	2.109	29.757	-0.463	-1.851	-0.457	-1.830	99.534	76.134
0.85	8.852	1.562	29.746	-0.377	-2.135	-0.364	-2.063	99.517	76.214
0.90	9.261	1.029	29.687	-0.275	-2.472	-0.258	-2.320	99.501	76.325
0.95	9.661	0.508	29.587	-0.151	-2.877	-0.137	-2.603	99.489	76.472
1.00	10.052	-0.000	29.452	0.000	-3.372	0.000	-2.916	99.485	76.661

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-5
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Tetrahydrofuran(2)
T: 25° C

Pure Component Volumes

V_1^o : 97.1473

V_2^o : 81.9426

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.588

υ_1 : 0.08895

υ_2 : 0.3255

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : 278.2234	g_{12} : -418.3542
λ_{21} : -279.1019	g_{21} : 378.3643
	α : 0.3080

This Study, Eq. 5-39

a : 0.02984

b : 0.08361

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	53.403	44.438	37.550	52.777	44.517	37.550	30.559	3.272
0.05	52.132	43.497	36.829	51.557	43.487	36.681	27.942	3.579
0.10	51.303	42.903	36.381	50.391	42.504	35.852	25.817	3.873
0.15	50.813	42.570	36.137	49.277	41.564	35.059	24.061	4.156
0.20	50.571	42.425	36.038	48.211	40.665	34.301	22.582	4.428
0.25	50.497	42.405	36.032	47.190	39.804	33.575	21.309	4.693
0.30	50.523	42.453	36.072	46.212	38.979	32.878	20.190	4.953
0.35	50.585	42.519	36.118	45.273	38.187	32.211	19.182	5.213
0.40	50.629	42.558	36.133	44.372	37.427	31.569	18.254	5.478
0.45	50.605	42.530	36.087	43.506	36.697	30.953	17.381	5.753
0.50	50.469	42.401	35.951	42.673	35.994	30.360	16.545	6.044
0.55	50.180	42.139	35.700	41.871	35.318	29.790	15.730	6.357
0.60	49.702	41.717	35.315	41.099	34.666	29.241	14.926	6.700
0.65	49.005	41.111	34.777	40.355	34.039	28.711	14.122	7.081
0.70	48.059	40.299	34.068	39.637	33.433	28.201	13.313	7.512
0.75	46.838	39.261	33.177	38.945	32.849	27.708	12.491	8.006
0.80	45.318	37.980	32.088	38.276	32.285	27.232	11.652	8.582
0.85	43.478	36.439	30.789	37.630	31.740	26.772	10.793	9.265
0.90	41.295	34.622	29.266	37.005	31.213	26.328	9.909	10.092
0.95	38.749	32.509	27.506	36.400	30.703	25.898	8.998	11.113
1.00	35.816	30.080	25.489	35.816	30.210	25.482	8.056	12.413

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-5 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	12.204	37.550	0.814	0.000	0.627	0.000	96.974	81.943
0.05	0.605	11.489	37.501	0.708	0.037	0.569	0.030	96.866	81.945
0.10	1.199	10.787	37.704	0.616	0.068	0.515	0.057	96.799	81.950
0.15	1.782	10.098	38.107	0.537	0.095	0.465	0.082	96.765	81.955
0.20	2.355	9.421	38.663	0.467	0.117	0.419	0.105	96.757	81.957
0.25	2.919	8.756	39.326	0.406	0.135	0.376	0.125	96.771	81.953
0.30	3.472	8.102	40.053	0.353	0.151	0.336	0.144	96.799	81.942
0.35	4.016	7.459	40.803	0.306	0.165	0.299	0.161	96.838	81.923
0.40	4.551	6.827	41.536	0.264	0.176	0.265	0.176	96.884	81.896
0.45	5.077	6.205	42.216	0.226	0.185	0.233	0.190	96.931	81.860
0.50	5.593	5.593	42.805	0.193	0.193	0.203	0.203	96.978	81.818
0.55	6.100	4.991	43.267	0.164	0.200	0.175	0.214	97.022	81.770
0.60	6.599	4.399	43.568	0.137	0.206	0.150	0.224	97.060	81.717
0.65	7.089	3.817	43.670	0.113	0.210	0.126	0.234	97.093	81.664
0.70	7.570	3.244	43.540	0.092	0.214	0.104	0.242	97.117	81.612
0.75	8.044	2.681	43.143	0.072	0.217	0.083	0.249	97.135	81.566
0.80	8.509	2.127	42.441	0.055	0.220	0.064	0.256	97.146	81.530
0.85	8.966	1.582	41.397	0.039	0.222	0.046	0.261	97.150	81.509
0.90	9.416	1.046	39.974	0.025	0.223	0.030	0.266	97.151	81.507
0.95	9.858	0.519	38.128	0.012	0.224	0.014	0.271	97.149	81.533
1.00	10.294	-0.000	35.816	-0.000	0.225	-0.000	0.274	97.147	81.591

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-6
Direct Correlation Function Integral Database
Carbon Tetrachloride(1) / Aniline(2)
T: 25° C

Pure Component Volumes

V_1^o : 97.1473

V_2^o : 91.6073

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -1.19

υ_1 : -0.107

υ_2 : 0.580

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†		NRTL, Eq. H-7,8	
λ_{12} :	269.3274	g_{12} :	866.0625
λ_{21} :	909.7982	g_{21} :	215.7150
		α :	0.3741

This Study, Eq. 5-39

a : -0.00745

b : 0.002348

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	85.011	82.935	78.787	88.604	83.551	78.787	-180.39	-0.554
0.05	81.499	79.565	75.561	82.523	77.817	73.379	-172.45	-0.580
0.10	78.268	76.419	72.497	77.222	72.819	68.666	-165.64	-0.604
0.15	75.254	73.444	69.554	72.562	68.424	64.522	-159.82	-0.626
0.20	72.403	70.598	66.699	68.432	64.529	60.849	-154.89	-0.646
0.25	69.673	67.849	63.910	64.747	61.054	57.573	-150.77	-0.663
0.30	67.033	65.175	61.169	61.438	57.934	54.631	-147.41	-0.678
0.35	64.460	62.558	58.467	58.451	55.118	51.975	-144.79	-0.691
0.40	61.937	59.990	55.796	55.741	52.563	49.565	-142.91	-0.700
0.45	59.455	57.465	53.155	53.271	50.234	47.369	-141.80	-0.705
0.50	57.011	54.982	50.544	51.011	48.102	45.359	-141.50	-0.707
0.55	54.603	52.546	47.964	48.935	46.144	43.513	-142.12	-0.704
0.60	52.236	50.162	45.417	47.021	44.340	41.811	-143.80	-0.695
0.65	49.917	47.835	42.901	45.252	42.671	40.238	-146.74	-0.681
0.70	47.654	45.576	40.414	43.610	41.123	38.778	-151.24	-0.661
0.75	45.457	43.390	37.946	42.084	39.684	37.421	-157.75	-0.634
0.80	43.337	41.284	35.476	40.660	38.342	36.155	-166.94	-0.599
0.85	41.305	39.261	32.964	39.330	37.088	34.973	-179.85	-0.556
0.90	39.370	37.318	30.339	38.085	35.913	33.865	-198.17	-0.505
0.95	37.539	35.439	27.469	36.915	34.810	32.825	-224.80	-0.445
1.00	35.816	33.588	24.097	35.816	33.773	31.847	-265.09	-0.377

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-6 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
				Wilson		NRTL			
0.00	0.000	10.916	78.787	-2.290	0.000	-1.814	0.000	96.430	91.607
0.05	0.544	10.343	75.957	-2.157	-0.114	-1.767	-0.093	96.326	91.610
0.10	1.086	9.774	73.261	-2.035	-0.226	-1.722	-0.191	96.282	91.613
0.15	1.625	9.208	70.674	-1.922	-0.339	-1.677	-0.296	96.286	91.612
0.20	2.161	8.644	68.175	-1.818	-0.454	-1.633	-0.408	96.327	91.603
0.25	2.694	8.083	65.747	-1.720	-0.573	-1.588	-0.529	96.396	91.583
0.30	3.225	7.524	63.379	-1.628	-0.698	-1.542	-0.661	96.484	91.550
0.35	3.752	6.968	61.062	-1.541	-0.830	-1.494	-0.805	96.582	91.502
0.40	4.276	6.414	58.792	-1.458	-0.972	-1.444	-0.963	96.684	91.441
0.45	4.797	5.863	56.564	-1.379	-1.128	-1.391	-1.138	96.783	91.367
0.50	5.315	5.315	54.380	-1.301	-1.301	-1.333	-1.333	96.877	91.283
0.55	5.829	4.769	52.241	-1.224	-1.496	-1.270	-1.552	96.959	91.192
0.60	6.339	4.226	50.149	-1.147	-1.720	-1.198	-1.797	97.029	91.097
0.65	6.845	3.686	48.110	-1.068	-1.983	-1.118	-2.076	97.084	91.006
0.70	7.348	3.149	46.129	-0.984	-2.295	-1.025	-2.392	97.124	90.923
0.75	7.847	2.616	44.212	-0.892	-2.676	-0.918	-2.753	97.150	90.856
0.80	8.343	2.086	42.366	-0.788	-3.152	-0.792	-3.168	97.162	90.815
0.85	8.835	1.559	40.596	-0.665	-3.766	-0.643	-3.646	97.164	90.808
0.90	9.324	1.036	38.910	-0.509	-4.584	-0.467	-4.201	97.159	90.846
0.95	9.810	0.516	37.314	-0.301	-5.723	-0.255	-4.848	97.151	90.940
1.00	10.294	-0.000	35.816	0.000	-7.401	0.000	-5.607	97.147	91.104

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-7
Direct Correlation Function Integral Database
Methanol(1) / Water(2)
T: 39.9° C

Pure Component Volumes

V_1^o : 41.4284

V_2^o : 18.1777

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -4.2149

υ_1 : -0.2225

υ_2 : 0.1049

υ_3 : 0.1838

υ_4 : 1.01166

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -34.8965

λ_{21} : 490.3911

NRTL, Eq. H-7,8

g_{12} : -127.5752

g_{21} : 580.8246

α : 0.3004

This Study, Eq. 5-39

a : -0.02667

b : -0.08229

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	64.835	31.840	15.115	78.511	34.449	15.115	-33.799	-2.959
0.05	58.735	29.139	13.916	60.961	26.748	11.736	-31.732	-3.151
0.10	54.707	27.112	12.889	49.824	21.861	9.592	-29.993	-3.334
0.15	51.600	25.347	11.901	42.127	18.484	8.110	-28.397	-3.521
0.20	48.813	23.648	10.906	36.490	16.011	7.025	-26.855	-3.724
0.25	46.055	21.941	9.903	32.184	14.122	6.196	-25.333	-3.947
0.30	43.222	20.222	8.910	28.787	12.631	5.542	-23.825	-4.197
0.35	40.315	18.517	7.951	26.038	11.425	5.013	-22.343	-4.476
0.40	37.383	16.857	7.042	23.769	10.429	4.576	-20.900	-4.785
0.45	34.488	15.271	6.196	21.863	9.593	4.209	-19.509	-5.126
0.50	31.683	13.775	5.416	20.241	8.881	3.897	-18.178	-5.501
0.55	29.005	12.377	4.699	18.842	8.267	3.628	-16.913	-5.913
0.60	26.475	11.076	4.041	17.625	7.733	3.393	-15.712	-6.365
0.65	24.097	9.869	3.437	16.555	7.264	3.187	-14.573	-6.862
0.70	21.869	8.751	2.885	15.607	6.848	3.005	-13.494	-7.411
0.75	19.784	7.723	2.384	14.762	6.477	2.842	-12.472	-8.018
0.80	17.838	6.787	1.937	14.004	6.145	2.696	-11.506	-8.691
0.85	16.034	5.954	1.550	13.320	5.845	2.564	-10.599	-9.435
0.90	14.382	5.238	1.229	12.700	5.572	2.445	-9.756	-10.250
0.95	12.900	4.658	0.985	12.135	5.324	2.336	-8.987	-11.127
1.00	11.618	4.240	0.832	11.618	5.098	2.237	-8.307	-12.037

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-7 Continued

x_1	ρ_1	ρ_2	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$	$\overline{V}_2$
	x 10^3 gmol/cc	x 10^3 gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	55.012	15.115	-2.236	0.000	-2.008	0.000	38.291	18.178
0.05	2.608	49.550	15.474	-1.948	-0.103	-1.802	-0.095	37.937	18.185
0.10	4.961	44.645	15.867	-1.701	-0.189	-1.612	-0.179	37.952	18.182
0.15	7.091	40.182	16.223	-1.488	-0.263	-1.439	-0.254	38.186	18.148
0.20	9.023	36.092	16.500	-1.302	-0.326	-1.281	-0.320	38.529	18.075
0.25	10.776	32.327	16.677	-1.139	-0.380	-1.136	-0.379	38.910	17.964
0.30	12.366	28.853	16.750	-0.996	-0.427	-1.003	-0.430	39.285	17.822
0.35	13.809	25.645	16.723	-0.868	-0.468	-0.882	-0.475	39.629	17.656
0.40	15.119	22.678	16.608	-0.755	-0.503	-0.771	-0.514	39.934	17.473
0.45	16.309	19.933	16.417	-0.654	-0.535	-0.670	-0.548	40.199	17.277
0.50	17.392	17.392	16.162	-0.562	-0.562	-0.577	-0.577	40.430	17.068
0.55	18.377	15.036	15.852	-0.480	-0.587	-0.492	-0.601	40.633	16.844
0.60	19.275	12.850	15.494	-0.406	-0.608	-0.415	-0.622	40.815	16.599
0.65	20.093	10.819	15.092	-0.338	-0.628	-0.344	-0.639	40.977	16.328
0.70	20.838	8.930	14.651	-0.276	-0.645	-0.280	-0.653	41.120	16.031
0.75	21.515	7.172	14.173	-0.220	-0.660	-0.221	-0.663	41.241	15.711
0.80	22.133	5.533	13.666	-0.168	-0.674	-0.168	-0.671	41.336	15.386
0.85	22.695	4.005	13.138	-0.121	-0.686	-0.119	-0.677	41.399	15.090
0.90	23.211	2.579	12.604	-0.077	-0.697	-0.076	-0.680	41.430	14.880
0.95	23.688	1.247	12.087	-0.037	-0.706	-0.036	-0.681	41.434	14.846
1.00	24.138	-0.000	11.618	0.000	-0.715	0.000	-0.680	41.428	15.118

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-8
Direct Correlation Function Integral Database
Chloroform(1) / Methanol(2)
T: 35° C

Pure Component Volumes

V_1^o : 81.7434

V_2^o : 41.1840

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.5490
υ_1 : -0.2727
υ_2 : 0.0
υ_3 : 0.0
υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -371.0661
λ_{21} : 1806.7567

NRTL, Eq. H-7,8

g_{12} : 1465.4611
g_{21} : -185.4119
α : 0.2907

This Study, Eq. 5-39

a : -0.06112
b : 0.06587

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	45.794	23.894	12.161	47.907	24.137	12.161	-14.042	-7.121
0.05	45.520	23.738	12.029	46.288	23.321	11.750	-15.932	-6.277
0.10	44.921	23.417	11.808	44.775	22.559	11.365	-17.931	-5.577
0.15	44.101	22.987	11.526	43.357	21.844	11.006	-20.071	-4.982
0.20	43.136	22.485	11.201	42.027	21.174	10.668	-22.388	-4.467
0.25	42.080	21.939	10.846	40.775	20.544	10.350	-24.928	-4.012
0.30	40.975	21.371	10.469	39.597	19.950	10.051	-27.746	-3.604
0.35	39.849	20.795	10.076	38.484	19.389	9.769	-30.912	-3.235
0.40	38.726	20.223	9.669	37.432	18.859	9.502	-34.517	-2.897
0.45	37.620	19.662	9.248	36.436	18.357	9.249	-38.682	-2.585
0.50	36.543	19.118	8.809	35.492	17.882	9.009	-43.571	-2.295
0.55	35.503	18.593	8.346	34.595	17.430	8.781	-49.410	-2.024
0.60	34.505	18.091	7.847	33.743	17.000	8.565	-56.526	-1.769
0.65	33.552	17.611	7.295	32.931	16.592	8.359	-65.406	-1.529
0.70	32.647	17.154	6.661	32.158	16.202	8.163	-76.804	-1.302
0.75	31.791	16.717	5.898	31.420	15.830	7.976	-91.957	-1.087
0.80	30.983	16.295	4.923	30.716	15.475	7.797	-113.02	-0.885
0.85	30.222	15.879	3.574	30.042	15.136	7.626	-144.12	-0.694
0.90	29.508	15.444	1.507	29.397	14.811	7.462	-194.05	-0.515
0.95	28.835	14.929	-2.157	28.779	14.500	7.305	-285.08	-0.351
1.00	28.187	14.106	-10.355	28.187	14.201	7.155	-490.86	-0.204

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-8 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	24.281	12.161	-1.155	0.000	-0.636	0.000	80.922	41.184
0.05	1.158	22.004	13.225	-1.144	-0.060	-0.687	-0.036	81.051	41.181
0.10	2.214	19.924	14.229	-1.134	-0.126	-0.738	-0.082	81.166	41.171
0.15	3.180	18.019	15.182	-1.124	-0.198	-0.790	-0.139	81.268	41.157
0.20	4.067	16.266	16.089	-1.113	-0.278	-0.841	-0.210	81.357	41.138
0.25	4.883	14.650	16.958	-1.102	-0.367	-0.891	-0.297	81.435	41.116
0.30	5.638	13.155	17.793	-1.092	-0.468	-0.940	-0.403	81.501	41.090
0.35	6.336	11.768	18.601	-1.080	-0.582	-0.986	-0.531	81.558	41.063
0.40	6.985	10.478	19.384	-1.068	-0.712	-1.029	-0.686	81.605	41.035
0.45	7.589	9.276	20.148	-1.056	-0.864	-1.067	-0.873	81.643	41.007
0.50	8.153	8.153	20.897	-1.043	-1.043	-1.099	-1.099	81.674	40.979
0.55	8.680	7.102	21.633	-1.028	-1.256	-1.122	-1.372	81.698	40.952
0.60	9.174	6.116	22.361	-1.011	-1.517	-1.134	-1.701	81.717	40.927
0.65	9.638	5.190	23.083	-0.992	-1.842	-1.130	-2.099	81.730	40.906
0.70	10.074	4.318	23.801	-0.968	-2.259	-1.106	-2.581	81.738	40.888
0.75	10.486	3.495	24.520	-0.938	-2.813	-1.056	-3.168	81.743	40.875
0.80	10.874	2.719	25.240	-0.896	-3.582	-0.971	-3.885	81.745	40.868
0.85	11.241	1.984	25.965	-0.833	-4.718	-0.841	-4.764	81.746	40.866
0.90	11.589	1.288	26.697	-0.727	-6.542	-0.650	-5.849	81.745	40.872
0.95	11.920	0.627	27.436	-0.520	-9.871	-0.379	-7.194	81.744	40.885
1.00	12.233	-0.000	28.187	0.000	-17.41	0.000	-8.876	81.743	40.908

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-9
Direct Correlation Function Integral Database
Chloroform(1) / Diethyl Ether(2)
T: 25° C

Pure Component Volumes

V_1^o : 80.6608

V_2^o :104.6655

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -5.547

υ_1 : -0.6303

υ_2 : 0.9545

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -104.7684

λ_{21} : -523.9499

NRTL, Eq. H-7,8

g_{12} : -410.0551

g_{21} : -245..5390f0

α : 0.3041

This Study, Eq. 5-39

a : 0.01638

b : -0.001507

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0	14.111	15.151	21.021	12.484	16.200	21.021	67.082	1.491
0.1257	14.927	17.156	23.989	13.519	17.542	22.762	63.783	1.568
0.2445	16.541	19.806	27.532	14.667	19.032	24.696	63.130	1.584
0.3567	18.746	22.941	31.501	15.947	20.692	26.851	64.221	1.557
0.4632	21.286	26.302	35.611	17.386	22.561	29.275	66.206	1.510
0.5641	23.955	29.689	39.663	19.012	24.671	32.013	68.667	1.456
0.6599	26.181	32.440	42.878	20.865	27.075	35.132	70.235	1.424
0.7511	28.058	34.746	45.575	22.999	29.844	38.725	71.469	1.399
0.8381	29.638	36.725	47.955	25.485	33.070	42.911	72.574	1.378
0.9209	30.885	38.369	50.043	28.408	36.862	47.832	73.442	1.362

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-9 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
1.00	31.903	39.830	52.054	31.903	41.397	53.717	74.223		1.347
0.0000	0.000	9.554	21.021	3.191	0.000	2.840	-0.000	75.438	104.67
0.1257	1.244	8.653	22.344	2.496	0.359	2.358	0.339	76.315	104.60
0.2445	2.501	7.728	24.021	1.986	0.643	1.951	0.631	77.357	104.36
0.3567	3.762	6.785	25.950	1.592	0.883	1.601	0.888	78.348	103.93
0.4632	5.026	5.825	27.908	1.273	1.099	1.296	1.118	79.181	103.35
0.5641	6.283	4.855	29.760	1.006	1.302	1.025	1.327	79.813	102.69
0.6599	7.529	3.880	30.922	0.772	1.499	0.783	1.520	80.243	102.01
0.7511	8.764	2.904	31.644	0.562	1.696	0.563	1.700	80.500	101.40
0.8381	9.988	1.929	32.041	0.367	1.898	0.361	1.870	80.622	100.94
0.9209	11.197	0.962	32.095	0.181	2.107	0.175	2.032	80.659	100.68
1.0000	12.398	0.000	31.903	0.000	2.327	-0.000	2.188	80.661	100.70

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-10
Direct Correlation Function Integral Database
Chloroform(1) / Acetone (2)
T: 25° C

Pure Component Volumes

V_1^o : 80.6608

V_2^o : 73.9308

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.3776
υ_1 : 0.9118
υ_2 : 0.0087
υ_3 : 0.0
υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -450.0211
λ_{21} : -117.0985

NRTL, Eq. H-7,8

g_{12} : -73.4242
g_{21} : -505.5625
α : 0.3069

This Study, Eq. 5-39

a : 0.02283
b : -0.01295

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	33.300	28.728	26.155	31.133	28.536	26.155	45.683	2.189
0.05	32.702	28.319	25.936	31.136	28.538	26.157	46.190	2.165
0.10	32.226	28.010	25.800	31.139	28.541	26.159	46.892	2.133
0.15	31.855	27.786	25.737	31.141	28.543	26.162	47.788	2.093
0.20	31.577	27.637	25.737	31.144	28.546	26.164	48.878	2.046
0.25	31.378	27.552	25.791	31.147	28.548	26.166	50.165	1.993
0.30	31.247	27.520	25.891	31.150	28.551	26.168	51.654	1.936
0.35	31.172	27.531	26.027	31.152	28.553	26.171	53.352	1.874
0.40	31.144	27.577	26.193	31.155	28.555	26.173	55.268	1.809
0.45	31.152	27.648	26.381	31.158	28.558	26.175	57.414	1.742
0.50	31.187	27.736	26.585	31.160	28.560	26.177	59.804	1.672
0.55	31.239	27.834	26.799	31.163	28.563	26.180	62.457	1.601
0.60	31.300	27.933	27.017	31.166	28.565	26.182	65.396	1.529
0.65	31.361	28.026	27.235	31.168	28.568	26.184	68.646	1.457
0.70	31.414	28.108	27.449	31.171	28.570	26.187	72.24	1.384
0.75	31.452	28.171	27.656	31.174	28.573	26.189	76.22	1.312
0.80	31.467	28.212	27.856	31.176	28.575	26.191	80.63	1.240
0.85	31.453	28.226	28.049	31.179	28.578	26.193	85.53	1.169
0.90	31.405	28.211	28.239	31.182	28.580	26.196	90.99	1.099
0.95	31.318	28.165	28.431	31.185	28.583	26.198	97.10	1.030
1.00	31.187	28.090	28.634	31.187	28.585	26.200	103.97	0.962

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-10 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	13.526	26.155	1.747	0.000	1.581	0.000	81.204	73.931
0.05	0.673	12.788	26.179	1.676	0.088	1.545	0.081	80.983	73.936
0.10	1.340	12.059	26.262	1.607	0.179	1.506	0.167	80.800	73.951
0.15	2.001	11.337	26.397	1.539	0.272	1.464	0.258	80.652	73.972
0.20	2.656	10.624	26.579	1.471	0.368	1.420	0.355	80.535	73.997
0.25	3.306	9.917	26.801	1.404	0.468	1.372	0.457	80.447	74.022
0.30	3.950	9.217	27.057	1.336	0.573	1.321	0.566	80.385	74.046
0.35	4.589	8.523	27.342	1.268	0.683	1.266	0.682	80.346	74.064
0.40	5.224	7.835	27.649	1.199	0.800	1.207	0.804	80.327	74.075
0.45	5.853	7.153	27.974	1.129	0.924	1.143	0.935	80.325	74.076
0.50	6.477	6.477	28.311	1.056	1.056	1.074	1.074	80.338	74.064
0.55	7.095	5.805	28.654	0.981	1.199	1.001	1.223	80.363	74.037
0.60	7.709	5.139	28.999	0.902	1.353	0.921	1.381	80.397	73.991
0.65	8.317	4.478	29.338	0.819	1.521	0.835	1.550	80.437	73.924
0.70	8.919	3.822	29.669	0.730	1.704	0.742	1.731	80.480	73.834
0.75	9.515	3.172	29.984	0.635	1.906	0.642	1.925	80.524	73.717
0.80	10.105	2.526	30.281	0.533	2.130	0.533	2.132	80.566	73.572
0.85	10.689	1.886	30.554	0.420	2.379	0.415	2.353	80.604	73.395
0.90	11.266	1.252	30.798	0.295	2.659	0.288	2.591	80.634	73.184
0.95	11.835	0.623	31.011	0.157	2.975	0.150	2.846	80.654	72.937
1.00	12.398	-0.000	31.187	-0.000	3.334	-0.000	3.120	80.661	72.650

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-11
Direct Correlation Function Integral Database
Carbon Disulfide(1) / Acetone(2)
T: 25° C

Pure Component Volumes

V_1^o : 60.6187

V_2^o : 73.9308

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 3.950

υ_1 : 0.3308

υ_2 : 0.7936

υ_3 : -0.2353

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 453.7602

λ_{21} : 955.994

NRTL, Eq. H-7,8

g_{12} : 1047.4373

g_{21} : 156.4837

α : 0.2913

This Study, Eq. 5-39

a : -0.01844

b : 0.01479

x_1	$(1\text{-}C_{11})$	$(1\text{-}C_{12})$	$(1\text{-}C_{22})$	$(1\text{-}C_{11})^{ID}$	$(1\text{-}C_{12})^{ID}$	$(1\text{-}C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	20.771	26.285	29.687	19.958	24.341	29.687	-74.239	-1.347
0.10	20.352	25.976	29.681	20.726	25.277	30.828	-70.697	-1.414
0.20	20.331	26.099	30.093	21.554	26.287	32.060	-69.332	-1.442
0.30	20.682	26.631	30.901	22.452	27.382	33.395	-70.118	-1.426
0.40	21.372	27.545	32.073	23.427	28.572	34.846	-73.271	-1.365
0.50	22.383	28.837	33.604	24.491	29.869	36.429	-79.421	-1.259
0.60	23.661	30.464	35.431	25.656	31.291	38.162	-89.716	-1.115
0.70	25.209	32.460	37.559	26.938	32.854	40.069	-106.82	-0.936
0.80	27.019	34.852	39.898	28.355	34.582	42.176	-136.65	-0.732
0.90	29.139	37.720	42.113	29.929	36.501	44.517	-195.63	-0.511
1.00	31.687	41.076	42.319	31.687	38.646	47.133	-346.24	-0.289

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-11 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	13.526	29.687	-2.501	0.000	-1.833	-0.000	65.458	73.931
0.10	1.370	12.326	28.921	-2.200	-0.244	-1.786	-0.198	64.160	73.997
0.20	2.779	11.116	28.425	-1.951	-0.488	-1.734	-0.434	63.161	74.172
0.30	4.236	9.884	28.188	-1.741	-0.746	-1.672	-0.717	62.423	74.416
0.40	5.749	8.624	28.188	-1.560	-1.040	-1.594	-1.063	61.897	74.697
0.50	7.325	7.325	28.416	-1.397	-1.397	-1.492	-1.492	61.524	75.001
0.60	8.971	5.981	28.810	-1.246	-1.868	-1.355	-2.033	61.248	75.337
0.70	10.696	4.584	29.365	-1.091	-2.546	-1.167	-2.724	61.028	75.748
0.80	12.513	3.128	30.041	-0.910	-3.639	-0.905	-3.619	60.838	76.323
0.90	14.437	1.604	30.813	-0.635	-5.714	-0.533	-4.797	60.687	77.200
1.00	16.497	0.000	31.687	0.000	-10.93	0.000	-6.371	60.619	78.579

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-12
Direct Correlation Function Integral Database
Acetonitrile(1) / Benzene(2)
T: 45° C

Pure Component Volumes

V_1^o : 54.1655

V_2^o : 91.6131

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.3996

υ_1 : -0.8195

υ_2 : -0.0745

υ_3 : 0.0658

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†		NRTL, Eq. H-7,8	
λ_{12} :	727.956	g_{12} :	309.9774
λ_{21} :	11.7755	g_{21} :	381.9848
		α :	0.2986

This Study, Eq. 5-39

a : -0.01413

b : -0.01539

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ $\times 10^2$
0.00	7.719	17.519	30.317	10.598	17.925	30.317	-72.866	-1.372
0.05	8.394	18.163	31.081	10.785	18.241	30.852	-69.000	-1.449
0.10	9.029	18.789	31.839	10.979	18.569	31.407	-65.554	-1.525
0.15	9.629	19.399	32.595	11.179	18.908	31.981	-62.472	-1.601
0.20	10.198	19.996	33.354	11.388	19.261	32.577	-59.707	-1.675
0.25	10.741	20.585	34.121	11.604	19.626	33.195	-57.222	-1.748
0.30	11.262	21.167	34.900	11.829	20.006	33.838	-54.983	-1.819
0.35	11.765	21.747	35.696	12.062	20.401	34.505	-52.963	-1.888
0.40	12.252	22.327	36.515	12.305	20.812	35.200	-51.137	-1.956
0.45	12.726	22.911	37.359	12.558	21.239	35.923	-49.484	-2.021
0.50	13.191	23.501	38.232	12.821	21.685	36.677	-47.983	-2.084
0.55	13.647	24.097	39.134	13.096	22.150	37.463	-46.613	-2.145
0.60	14.094	24.698	40.061	13.382	22.634	38.283	-45.352	-2.205
0.65	14.532	25.299	41.005	13.682	23.141	39.140	-44.178	-2.264
0.70	14.955	25.892	41.950	13.995	23.671	40.036	-43.063	-2.322
0.75	15.356	26.462	42.868	14.323	24.226	40.974	-41.975	-2.382
0.80	15.722	26.984	43.716	14.667	24.807	41.958	-40.875	-2.447
0.85	16.031	27.422	44.429	15.028	25.417	42.989	-39.710	-2.518
0.90	16.253	27.719	44.909	15.406	26.058	44.073	-38.415	-2.603
0.95	16.340	27.793	45.014	15.805	26.731	45.212	-36.901	-2.710
1.00	16.224	27.525	44.536	16.224	27.441	46.412	-35.051	-2.853

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-12 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	10.915	30.317	-2.403	0.000	-2.179	-0.000	52.938	91.613
0.05	0.557	10.592	29.797	-2.200	-0.116	-2.045	-0.108	53.200	91.606
0.10	1.139	10.254	29.262	-2.016	-0.224	-1.915	-0.213	53.431	91.588
0.15	1.747	9.899	28.713	-1.849	-0.326	-1.789	-0.316	53.632	91.559
0.20	2.382	9.526	28.154	-1.697	-0.424	-1.667	-0.417	53.801	91.523
0.25	3.045	9.135	27.584	-1.556	-0.519	-1.548	-0.516	53.942	91.483
0.30	3.740	8.726	27.005	-1.425	-0.611	-1.433	-0.614	54.054	91.440
0.35	4.467	8.295	26.418	-1.303	-0.702	-1.320	-0.711	54.141	91.399
0.40	5.229	7.843	25.823	-1.188	-0.792	-1.211	-0.807	54.204	91.361
0.45	6.029	7.368	25.219	-1.079	-0.883	-1.103	-0.902	54.246	91.330
0.50	6.869	6.869	24.606	-0.975	-0.975	-0.998	-0.998	54.270	91.308
0.55	7.753	6.344	23.981	-0.875	-1.069	-0.894	-1.092	54.280	91.298
0.60	8.685	5.790	23.339	-0.777	-1.166	-0.792	-1.187	54.277	91.302
0.65	9.668	5.206	22.674	-0.682	-1.266	-0.691	-1.283	54.266	91.321
0.70	10.706	4.588	21.978	-0.588	-1.372	-0.591	-1.379	54.249	91.356
0.75	11.807	3.936	21.240	-0.494	-1.482	-0.492	-1.475	54.230	91.408
0.80	12.974	3.243	20.445	-0.400	-1.599	-0.393	-1.573	54.210	91.477
0.85	14.215	2.508	19.575	-0.304	-1.724	-0.295	-1.672	54.192	91.562
0.90	15.537	1.726	18.603	-0.206	-1.858	-0.197	-1.772	54.178	91.662
0.95	16.950	0.892	17.500	-0.105	-2.003	-0.099	-1.874	54.169	91.773
1.00	18.462	-0.000	16.224	0.000	-2.160	0.000	-1.978	54.166	91.893

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-13
Direct Correlation Function Integral Database
Dichloroethane(1) / Benzene(2)
T: 20° C

Pure Component Volumes

V_1^o : 78.9848

V_2^o : 89.0004

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 1.0

υ_1 : -0.14

υ_2 : 0.17

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 235.0871

λ_{21} : -192.4128

NRTL, Eq. H-7,8

g_{12} : -89.3581

g_{21} : 120.4722

α : 0.3278

This Study, Eq. 5-39

a : -0.1440

b : -0.3381

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0	37.582	41.950	46.661	36.750	41.410	46.661	-6.186	-16.165
0.2	35.907	40.266	45.023	36.147	40.731	45.896	-4.700	-21.275
0.4	35.400	39.823	44.695	35.564	40.074	45.156	-3.689	-27.110
0.6	35.024	39.532	44.538	35.000	39.438	44.439	-2.913	-34.325
0.8	34.638	39.293	44.506	34.453	38.822	43.745	-2.305	-43.376
1.00	33.923	38.788	44.296	33.923	38.225	43.072	-1.805	-55.394

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-13 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	11.236	46.661	-0.133	0.000	-0.103	0.000	80.015	89.000
0.20	2.295	9.179	43.136	-0.087	-0.022	-0.076	-0.019	79.594	89.044
0.40	4.693	7.040	40.870	-0.054	-0.036	-0.053	-0.035	79.358	89.143
0.60	7.208	4.805	38.710	-0.030	-0.045	-0.033	-0.049	79.190	89.313
0.80	9.856	2.464	36.523	-0.013	-0.050	-0.015	-0.060	79.053	89.645
1.00	12.661	0.000	33.923	0.000	-0.053	0.000	-0.069	78.985	90.310

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-14
Direct Correlation Function Integral Database
Ethanol(1) / Cyclohexane(2)
T: 10° C

Pure Component Volumes

V_1^o : 57.5158

V_2^o :107.0220

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 1.9378

υ_1 : -0.2995

υ_2 : 0.6529

υ_3 : 0.4060

υ_4 : 0.3162

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 2080.7615

λ_{21} : 461.9340

NRTL, Eq. H-7,8

g_{12} : 853.3773

g_{21} : 1373.5519

α : 0.4456

This Study, Eq. 5-39

a : -0.001015

b : -0.01198

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	-28.268	24.893	44.014	12.712	23.654	44.014	-1863.9	-0.054
0.05	-0.756	25.561	44.413	13.030	24.245	45.114	-686.94	-0.146
0.10	5.683	25.817	45.012	13.364	24.867	46.271	-410.71	-0.243
0.15	8.514	26.148	45.770	13.716	25.522	47.489	-294.02	-0.340
0.20	10.183	26.574	46.649	14.087	26.211	48.773	-231.18	-0.433
0.25	11.357	27.082	47.624	14.478	26.940	50.128	-192.59	-0.519
0.30	12.282	27.656	48.685	14.892	27.709	51.560	-166.91	-0.599
0.35	13.069	28.287	49.827	15.330	28.524	53.077	-148.97	-0.671
0.40	13.777	28.973	51.058	15.794	29.389	54.685	-136.06	-0.735
0.45	14.439	29.717	52.389	16.288	30.307	56.394	-126.68	-0.789
0.50	15.080	30.526	53.840	16.813	31.285	58.214	-119.96	-0.834
0.55	15.721	31.414	55.432	17.374	32.328	60.154	-115.38	-0.867
0.60	16.379	32.395	57.194	17.973	33.443	62.229	-112.64	-0.888
0.65	17.072	33.490	59.159	18.615	34.638	64.452	-111.62	-0.896
0.70	17.817	34.723	61.365	19.305	35.921	66.839	-112.35	-0.890
0.75	18.634	36.123	63.858	20.047	37.302	69.410	-114.99	-0.870
0.80	19.545	37.728	66.692	20.849	38.795	72.187	-119.90	-0.834
0.85	20.578	39.584	69.937	21.718	40.411	75.195	-127.74	-0.783
0.90	21.767	41.753	73.678	22.662	42.169	78.465	-139.62	-0.716
0.95	23.159	44.320	78.012	23.693	44.086	82.032	-157.52	-0.635
1.00	24.821	47.394	83.039	24.821	46.186	85.939	-185.07	-0.540

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-14 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\bar{V}_1$	$\bar{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	9.344	44.014	-42.35	0.000	-15.28	-0.000	60.529	107.02
0.05	0.478	9.076	42.509	-15.35	-0.808	-11.19	-0.589	59.702	107.04
0.10	0.978	8.798	41.164	-8.980	-0.998	-8.430	-0.937	59.151	107.09
0.15	1.502	8.510	39.928	-6.259	-1.105	-6.509	-1.149	58.794	107.14
0.20	2.052	8.208	38.766	-4.771	-1.193	-5.140	-1.285	58.568	107.18
0.25	2.631	7.893	37.654	-3.836	-1.279	-4.145	-1.382	58.424	107.22
0.30	3.240	7.561	36.576	-3.194	-1.369	-3.408	-1.461	58.328	107.26
0.35	3.883	7.212	35.524	-2.726	-1.468	-2.854	-1.537	58.257	107.29
0.40	4.562	6.843	34.492	-2.367	-1.578	-2.431	-1.621	58.197	107.33
0.45	5.281	6.454	33.482	-2.081	-1.703	-2.103	-1.720	58.137	107.38
0.50	6.042	6.042	32.493	-1.846	-1.846	-1.842	-1.842	58.075	107.43
0.55	6.851	5.605	31.530	-1.647	-2.013	-1.631	-1.994	58.009	107.50
0.60	7.712	5.141	30.597	-1.473	-2.209	-1.454	-2.181	57.939	107.60
0.65	8.630	4.647	29.698	-1.316	-2.443	-1.300	-2.414	57.868	107.72
0.70	9.613	4.120	28.837	-1.169	-2.727	-1.157	-2.701	57.798	107.86
0.75	10.667	3.556	28.019	-1.026	-3.078	-1.018	-3.054	57.730	108.04
0.80	11.802	2.950	27.249	-0.880	-3.520	-0.872	-3.488	57.667	108.26
0.85	13.027	2.299	26.535	-0.722	-4.092	-0.710	-4.023	57.610	108.53
0.90	14.356	1.595	25.883	-0.539	-4.855	-0.520	-4.683	57.563	108.86
0.95	15.803	0.832	25.307	-0.311	-5.913	-0.289	-5.500	57.529	109.28
1.00	17.387	-0.000	24.821	0.000	-7.456	0.000	-6.518	57.516	109.82

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-15
Direct Correlation Function Integral Database
Ethanol(1) / Benzene(2)
T: 25° C

Pure Component Volumes

V_1^o : 58.5159

V_2^o : 89.5022

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 0.09871f0

υ_1 : 0.5741

υ_2 : 0.03247f0

υ_3 : 0.3793

υ_4 : 0.3591

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : 1671.2618	g_{12} : 563.827
λ_{21} : 175.9216	g_{21} : 1293.2086
	α : 0.5139

This Study, Eq. 5-39

a : -0.001591

b : 0.01844

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	-4.414	24.346	36.342	15.534	23.760	36.342	-753.17	-0.133
0.05	5.170	24.560	36.179	15.751	24.091	36.848	-416.13	-0.240
0.10	8.961	24.603	36.170	15.973	24.431	37.369	-281.17	-0.356
0.15	10.973	24.685	36.282	16.202	24.782	37.904	-211.20	-0.473
0.20	12.256	24.829	36.484	16.438	25.142	38.455	-169.30	-0.591
0.25	13.184	25.028	36.757	16.680	25.513	39.023	-141.81	-0.705
0.30	13.918	25.276	37.091	16.930	25.895	39.607	-122.62	-0.816
0.35	14.539	25.566	37.483	17.187	26.288	40.209	-108.64	-0.920
0.40	15.093	25.897	37.934	17.452	26.694	40.829	-98.129	-1.019
0.45	15.608	26.271	38.447	17.726	27.112	41.469	-90.064	-1.110
0.50	16.105	26.688	39.023	18.008	27.544	42.130	-83.793	-1.193
0.55	16.599	27.153	39.663	18.300	27.990	42.812	-78.886	-1.268
0.60	17.100	27.664	40.364	18.601	28.450	43.516	-75.051	-1.332
0.65	17.614	28.219	41.118	18.912	28.926	44.244	-72.078	-1.387
0.70	18.144	28.814	41.911	19.233	29.418	44.996	-69.816	-1.432
0.75	18.689	29.440	42.728	19.566	29.927	45.775	-68.152	-1.467
0.80	19.245	30.084	43.546	19.911	30.454	46.581	-67.003	-1.492
0.85	19.804	30.733	44.345	20.268	31.000	47.416	-66.305	-1.508
0.90	20.358	31.373	45.105	20.638	31.566	48.281	-66.015	-1.515
0.95	20.899	31.994	45.817	21.021	32.153	49.179	-66.109	-1.513
1.00	21.419	32.592	46.485	21.419	32.762	50.110	-66.581	-1.502

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-15 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	11.173	36.342	-20.72	0.000	-14.12	0.000	59.960	89.502
0.05	0.568	10.795	34.997	-11.30	-0.595	-10.20	-0.537	59.322	89.517
0.10	1.156	10.406	33.816	-7.483	-0.831	-7.585	-0.843	58.923	89.549
0.15	1.766	10.006	32.755	-5.481	-0.967	-5.790	-1.022	58.683	89.583
0.20	2.398	9.593	31.785	-4.261	-1.065	-4.522	-1.130	58.548	89.611
0.25	3.055	9.164	30.886	-3.444	-1.148	-3.605	-1.202	58.476	89.632
0.30	3.737	8.719	30.043	-2.857	-1.224	-2.928	-1.255	58.439	89.645
0.35	4.446	8.257	29.250	-2.414	-1.300	-2.418	-1.302	58.420	89.654
0.40	5.184	7.776	28.502	-2.066	-1.377	-2.027	-1.352	58.409	89.661
0.45	5.953	7.275	27.795	-1.782	-1.458	-1.722	-1.409	58.402	89.666
0.50	6.754	6.754	27.126	-1.544	-1.544	-1.477	-1.477	58.397	89.670
0.55	7.589	6.209	26.494	-1.340	-1.638	-1.277	-1.560	58.396	89.672
0.60	8.462	5.641	25.893	-1.159	-1.739	-1.108	-1.662	58.399	89.667
0.65	9.374	5.047	25.319	-0.996	-1.850	-0.961	-1.784	58.408	89.652
0.70	10.327	4.426	24.764	-0.846	-1.973	-0.827	-1.931	58.423	89.621
0.75	11.325	3.775	24.223	-0.703	-2.110	-0.702	-2.105	58.442	89.569
0.80	12.370	3.093	23.685	-0.566	-2.263	-0.578	-2.311	58.465	89.492
0.85	13.466	2.376	23.143	-0.430	-2.435	-0.451	-2.554	58.486	89.392
0.90	14.615	1.624	22.588	-0.292	-2.630	-0.315	-2.839	58.503	89.272
0.95	15.822	0.833	22.015	-0.150	-2.853	-0.167	-3.174	58.513	89.147
1.00	17.089	-0.000	21.419	0.000	-3.108	0.000	-3.567	58.516	89.039

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-16
Direct Correlation Function Integral Database
Ethanol(1) / Heptane(2)
T: 30° C

Pure Component Volumes

V_1^o : 58.8643

V_2^o :148.0431

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 1.8932
υ_1 : -0.00524
υ_2 : 0.6420
υ_3 : 0.4527
υ_4 : 0.9566

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 2316.8963
λ_{21} : 422.9376

NRTL, Eq. H-7,8

g_{12} : 1101.3813
g_{21} : 1534.9774
α : 0.4634

This Study, Eq. 5-39

a : -0.001399
b : -0.01252

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	-29.086	16.760	39.507	6.246	15.709	39.507	-1430.0	-0.070
0.05	-6.891	17.518	40.419	6.470	16.273	40.927	-585.40	-0.171
0.10	-0.922	17.925	41.572	6.712	16.879	42.452	-359.65	-0.278
0.15	1.828	18.407	42.930	6.971	17.533	44.095	-260.33	-0.384
0.20	3.479	18.988	44.463	7.252	18.239	45.870	-205.84	-0.486
0.25	4.646	19.659	46.157	7.556	19.004	47.795	-172.01	-0.581
0.30	5.567	20.412	48.014	7.887	19.836	49.888	-149.35	-0.670
0.35	6.351	21.244	50.050	8.248	20.745	52.172	-133.45	-0.749
0.40	7.060	22.161	52.289	8.644	21.740	54.676	-121.99	-0.820
0.45	7.731	23.175	54.768	9.080	22.836	57.433	-113.67	-0.880
0.50	8.394	24.303	57.531	9.562	24.049	60.482	-107.73	-0.928
0.55	9.071	25.568	60.630	10.098	25.397	63.873	-103.73	-0.964
0.60	9.784	26.997	64.126	10.698	26.905	67.667	-101.42	-0.986
0.65	10.554	28.624	68.094	11.374	28.604	71.940	-100.73	-0.993
0.70	11.401	30.491	72.627	12.140	30.533	76.789	-101.69	-0.983
0.75	12.350	32.649	77.850	13.018	32.739	82.339	-104.53	-0.957
0.80	13.432	35.173	83.940	14.032	35.290	88.754	-109.71	-0.912
0.85	14.688	38.172	91.163	15.217	38.272	96.253	-118.05	-0.847
0.90	16.184	41.814	99.931	16.622	41.804	105.135	-131.10	-0.763
0.95	18.024	46.376	110.904	18.312	46.054	115.825	-151.83	-0.659
1.00	20.384	52.320	125.142	20.384	51.266	128.933	-186.47	-0.536

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-16 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	6.755	39.507	-36.20	0.000	-17.27	0.000	62.804	148.04
0.05	0.348	6.609	38.125	-14.59	-0.768	-12.14	-0.639	61.447	148.08
0.10	0.717	6.457	36.891	-8.774	-0.975	-8.834	-0.982	60.609	148.14
0.15	1.111	6.296	35.752	-6.189	-1.092	-6.630	-1.170	60.113	148.21
0.20	1.532	6.126	34.671	-4.749	-1.187	-5.117	-1.279	59.831	148.27
0.25	1.982	5.945	33.626	-3.837	-1.279	-4.052	-1.351	59.674	148.31
0.30	2.465	5.751	32.601	-3.207	-1.374	-3.290	-1.410	59.582	148.35
0.35	2.984	5.542	31.590	-2.746	-1.479	-2.734	-1.472	59.517	148.38
0.40	3.545	5.318	30.591	-2.393	-1.595	-2.323	-1.549	59.460	148.42
0.45	4.152	5.075	29.605	-2.112	-1.728	-2.016	-1.649	59.401	148.46
0.50	4.811	4.811	28.633	-1.881	-1.881	-1.782	-1.782	59.339	148.52
0.55	5.530	4.524	27.678	-1.687	-2.061	-1.601	-1.957	59.277	148.58
0.60	6.316	4.211	26.741	-1.517	-2.276	-1.456	-2.183	59.217	148.66
0.65	7.181	3.867	25.825	-1.365	-2.535	-1.333	-2.476	59.162	148.76
0.70	8.136	3.487	24.929	-1.224	-2.855	-1.223	-2.853	59.113	148.86
0.75	9.197	3.066	24.056	-1.086	-3.259	-1.112	-3.337	59.067	148.98
0.80	10.384	2.596	23.209	-0.945	-3.781	-0.990	-3.960	59.022	149.14
0.85	11.719	2.068	22.397	-0.791	-4.480	-0.841	-4.765	58.975	149.36
0.90	13.234	1.470	21.635	-0.606	-5.454	-0.646	-5.812	58.927	149.70
0.95	14.972	0.788	20.950	-0.362	-6.885	-0.378	-7.187	58.885	150.24
1.00	16.988	-0.000	20.384	0.000	-9.148	0.000	-9.013	58.864	151.09

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-17
Direct Correlation Function Integral Database
Ethanol(1) / Water(2)
T: 40° C

Pure Component Volumes

V_1^o : 59.5884

V_2^o : 18.1781

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -4.0659

υ_1 : -0.9813

υ_2 : -2.0256

υ_3 : -0.0848

υ_4 : 1.5930

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 173.3876

λ_{21} : 890.3253

NRTL, Eq. H-7,8

g_{12} : -13.6137

g_{21} : 1004.3349

α : 0.2946

This Study, Eq. 5-39

a : -0.01074

b : -0.03195

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	126.438	44.916	15.113	162.401	49.542	15.113	-106.53	-0.939
0.05	118.139	41.322	13.655	116.797	35.630	10.869	-94.231	-1.061
0.10	110.115	37.752	12.173	91.190	27.818	8.486	-84.725	-1.180
0.15	101.800	34.135	10.691	74.792	22.816	6.960	-76.881	-1.301
0.20	93.198	30.562	9.269	63.393	19.339	5.899	-70.183	-1.425
0.25	84.566	27.159	7.961	55.009	16.781	5.119	-64.377	-1.553
0.30	76.216	24.034	6.801	48.583	14.821	4.521	-59.327	-1.686
0.35	68.407	21.249	5.797	43.502	13.271	4.048	-54.941	-1.820
0.40	61.303	18.817	4.941	39.383	12.014	3.665	-51.142	-1.955
0.45	54.973	16.718	4.214	35.976	10.975	3.348	-47.857	-2.090
0.50	49.410	14.911	3.589	33.112	10.101	3.082	-45.013	-2.222
0.55	44.554	13.342	3.041	30.671	9.356	2.854	-42.539	-2.351
0.60	40.312	11.961	2.547	28.564	8.714	2.658	-40.362	-2.478
0.65	36.582	10.718	2.090	26.729	8.154	2.487	-38.416	-2.603
0.70	33.262	9.576	1.655	25.115	7.662	2.337	-36.639	-2.729
0.75	30.260	8.512	1.238	23.685	7.225	2.204	-34.978	-2.859
0.80	27.504	7.515	0.839	22.409	6.836	2.085	-33.392	-2.995
0.85	24.949	6.595	0.466	21.263	6.486	1.979	-31.856	-3.139
0.90	22.574	5.771	0.130	20.229	6.171	1.883	-30.365	-3.293
0.95	20.390	5.079	-0.154	19.291	5.885	1.795	-28.939	-3.456
1.00	18.436	4.562	-0.369	18.436	5.624	1.716	-27.624	-3.620

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-17 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	55.011	15.113	-7.049	0.000	-5.149	0.000	54.024	18.178
0.05	2.502	47.542	16.545	-5.411	-0.285	-4.467	-0.235	54.546	18.163
0.10	4.583	41.245	17.757	-4.294	-0.477	-3.875	-0.431	55.284	18.103
0.15	6.329	35.862	18.719	-3.491	-0.616	-3.359	-0.593	56.073	17.990
0.20	7.804	31.215	19.440	-2.888	-0.722	-2.908	-0.727	56.808	17.834
0.25	9.059	27.176	19.948	-2.420	-0.807	-2.513	-0.838	57.430	17.654
0.30	10.134	23.645	20.286	-2.047	-0.877	-2.167	-0.929	57.919	17.469
0.35	11.062	20.543	20.497	-1.742	-0.938	-1.862	-1.003	58.279	17.297
0.40	11.869	17.804	20.619	-1.488	-0.992	-1.594	-1.063	58.530	17.147
0.45	12.578	15.373	20.682	-1.273	-1.041	-1.357	-1.111	58.699	17.023
0.50	13.204	13.204	20.705	-1.087	-1.087	-1.148	-1.148	58.817	16.916
0.55	13.761	11.259	20.698	-0.925	-1.130	-0.963	-1.177	58.911	16.813
0.60	14.260	9.506	20.661	-0.781	-1.172	-0.799	-1.198	59.001	16.690
0.65	14.706	7.919	20.588	-0.653	-1.213	-0.653	-1.213	59.100	16.526
0.70	15.107	6.475	20.469	-0.537	-1.253	-0.524	-1.223	59.209	16.298
0.75	15.467	5.156	20.290	-0.431	-1.293	-0.409	-1.228	59.323	15.996
0.80	15.789	3.947	20.041	-0.333	-1.333	-0.307	-1.229	59.430	15.625
0.85	16.077	2.837	19.717	-0.242	-1.373	-0.216	-1.226	59.517	15.218
0.90	16.335	1.815	19.325	-0.157	-1.414	-0.136	-1.221	59.571	14.845
0.95	16.567	0.872	18.884	-0.077	-1.456	-0.064	-1.213	59.589	14.627
1.00	16.782	-0.000	18.436	0.000	-1.498	0.000	-1.204	59.588	14.746

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-18
Direct Correlation Function Integral Database
Acetone(1) / Benzene(2)
T: 25° C

Pure Component Volumes

V_1^o : 73.9308

V_2^o : 89.5022

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.2887

υ_1 : -0.0263

υ_2 : 0.0894

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 418.0568

λ_{21} : -104.7155

NRTL, Eq. H-7,8

g_{12} : -70.4352

g_{21} : 384.0653

α : 0.3029

This Study, Eq. 5-39

a : -0.01864

b : -0.03436

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	23.271	29.928	36.342	24.797	30.019	36.342	-49.937	-2.003
0.05	24.461	31.202	37.812	24.861	30.097	36.437	-48.635	-2.056
0.10	25.590	32.414	39.211	24.926	30.176	36.532	-47.298	-2.114
0.15	26.649	33.554	40.525	24.991	30.255	36.627	-45.921	-2.178
0.20	27.631	34.609	41.738	25.057	30.334	36.723	-44.502	-2.247
0.25	28.527	35.568	42.837	25.123	30.414	36.820	-43.041	-2.323
0.30	29.327	36.418	43.807	25.189	30.494	36.917	-41.536	-2.408
0.35	30.023	37.148	44.632	25.256	30.575	37.015	-39.988	-2.501
0.40	30.604	37.746	45.299	25.323	30.656	37.113	-38.398	-2.604
0.45	31.062	38.200	45.795	25.390	30.738	37.212	-36.769	-2.720
0.50	31.387	38.500	46.107	25.458	30.820	37.311	-35.103	-2.849
0.55	31.572	38.636	46.224	25.526	30.902	37.411	-33.405	-2.994
0.60	31.609	38.601	46.137	25.594	30.985	37.511	-31.679	-3.157
0.65	31.492	38.385	45.837	25.663	31.068	37.612	-29.929	-3.341
0.70	31.217	37.985	45.318	25.732	31.152	37.713	-28.162	-3.551
0.75	30.779	37.395	44.576	25.802	31.236	37.815	-26.383	-3.790
0.80	30.178	36.614	43.608	25.871	31.320	37.917	-24.600	-4.065
0.85	29.413	35.642	42.414	25.942	31.406	38.020	-22.820	-4.382
0.90	28.484	34.480	40.997	26.012	31.491	38.124	-21.049	-4.751
0.95	27.397	33.131	39.361	26.083	31.577	38.228	-19.295	-5.183
1.00	26.155	31.602	37.513	26.155	31.664	38.333	-17.566	-5.693

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-18 Continued

x_1	ρ_1	ρ_2	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$	$\overline{V}_2$
	x 10^3	x 10^3							
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	11.173	36.342	-1.374	0.000	-1.322	0.000	73.705	89.502
0.05	0.564	10.709	37.151	-1.244	-0.065	-1.210	-0.064	73.702	89.502
0.10	1.137	10.236	37.852	-1.125	-0.125	-1.104	-0.123	73.707	89.502
0.15	1.722	9.755	38.435	-1.016	-0.179	-1.005	-0.177	73.719	89.500
0.20	2.316	9.265	38.893	-0.915	-0.229	-0.911	-0.228	73.736	89.496
0.25	2.922	8.766	39.217	-0.823	-0.274	-0.824	-0.275	73.756	89.491
0.30	3.539	8.258	39.400	-0.738	-0.316	-0.741	-0.318	73.778	89.482
0.35	4.167	7.739	39.437	-0.659	-0.355	-0.664	-0.357	73.801	89.471
0.40	4.807	7.211	39.322	-0.586	-0.391	-0.591	-0.394	73.824	89.458
0.45	5.460	6.673	39.052	-0.518	-0.424	-0.522	-0.427	73.845	89.442
0.50	6.124	6.124	38.624	-0.454	-0.454	-0.458	-0.458	73.865	89.423
0.55	6.801	5.565	38.036	-0.395	-0.483	-0.398	-0.486	73.883	89.404
0.60	7.491	4.994	37.289	-0.340	-0.510	-0.341	-0.512	73.898	89.384
0.65	8.195	4.413	36.386	-0.288	-0.535	-0.288	-0.536	73.910	89.363
0.70	8.912	3.819	35.328	-0.239	-0.558	-0.239	-0.557	73.919	89.344
0.75	9.643	3.214	34.122	-0.193	-0.580	-0.192	-0.576	73.926	89.327
0.80	10.389	2.597	32.775	-0.150	-0.600	-0.148	-0.594	73.930	89.314
0.85	11.149	1.968	31.294	-0.109	-0.620	-0.107	-0.609	73.931	89.306
0.90	11.925	1.325	29.689	-0.071	-0.638	-0.069	-0.623	73.932	89.304
0.95	12.717	0.669	27.971	-0.034	-0.655	-0.033	-0.635	73.931	89.311
1.00	13.526	-0.000	26.155	0.000	-0.672	0.000	-0.646	73.931	89.329

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-19
Direct Correlation Function Integral Database
Acetone(1) / Water(2)
T: 25° C

Pure Component Volumes

V_1^o : 73.9308

V_2^o : 18.1053

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -5.7362
υ_1 : -2.105
υ_2 : -1.422
υ_3 : -0.4402
υ_4 : 1.527

Activity Coefficient Parameters

Wilson, Eq. H-3,4†
λ_{12} : -107.3231
λ_{21} : 1582.008

NRTL, Eq. H-7,8
g_{12} : 431.8749
g_{21} : 787.9978
α : 0.2915

This Study, Eq. 5-39
a : -0.01740
b : 0.007957

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	197.886	56.066	15.438	257.407	63.038	15.438	-88.514	-1.130
0.05	189.396	52.777	14.220	178.496	43.713	10.705	-92.117	-1.086
0.10	178.286	48.644	12.744	136.616	33.457	8.193	-94.117	-1.063
0.15	165.257	44.035	11.159	110.653	27.098	6.636	-94.940	-1.053
0.20	151.176	39.311	9.594	92.983	22.771	5.577	-94.988	-1.053
0.25	136.871	34.757	8.135	80.179	19.635	4.809	-94.609	-1.057
0.30	123.007	30.561	6.828	70.474	17.259	4.227	-94.087	-1.063
0.35	110.035	26.816	5.684	62.865	15.395	3.770	-93.646	-1.068
0.40	98.210	23.543	4.692	56.739	13.895	3.403	-93.452	-1.070
0.45	87.621	20.715	3.829	51.701	12.661	3.101	-93.631	-1.068
0.50	78.245	18.276	3.064	47.485	11.629	2.848	-94.275	-1.061
0.55	69.983	16.163	2.369	43.904	10.752	2.633	-95.455	-1.048
0.60	62.702	14.313	1.716	40.826	9.998	2.448	-97.235	-1.028
0.65	56.255	12.670	1.082	38.151	9.343	2.288	-99.684	-1.003
0.70	50.504	11.195	0.444	35.805	8.768	2.147	-102.89	-0.972
0.75	45.329	9.859	-0.216	33.731	8.260	2.023	-106.99	-0.935
0.80	40.641	8.654	-0.918	31.884	7.808	1.912	-112.21	-0.891
0.85	36.383	7.581	-1.688	30.228	7.403	1.813	-118.90	-0.841
0.90	32.535	6.655	-2.563	28.736	7.037	1.723	-127.68	-0.783
0.95	29.110	5.893	-3.603	27.385	6.706	1.642	-139.62	-0.716
1.00	26.155	5.313	-4.910	26.155	6.405	1.569	-156.65	-0.638

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-19 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	55.232	15.438	-5.734	0.000	-4.873	0.000	65.754	18.105
0.05	2.438	46.315	18.321	-4.777	-0.251	-4.404	-0.232	66.735	18.079
0.10	4.353	39.174	20.861	-4.060	-0.451	-3.980	-0.442	67.847	17.988
0.15	5.883	33.335	23.010	-3.507	-0.619	-3.596	-0.635	68.948	17.831
0.20	7.121	28.485	24.766	-3.068	-0.767	-3.248	-0.812	69.949	17.619
0.25	8.135	24.406	26.164	-2.712	-0.904	-2.930	-0.977	70.805	17.371
0.30	8.975	20.942	27.252	-2.417	-1.036	-2.639	-1.131	71.502	17.108
0.35	9.677	17.972	28.082	-2.168	-1.167	-2.371	-1.277	72.048	16.846
0.40	10.271	15.407	28.703	-1.953	-1.302	-2.124	-1.416	72.465	16.597
0.45	10.778	13.173	29.155	-1.766	-1.445	-1.895	-1.550	72.780	16.364
0.50	11.215	11.215	29.465	-1.600	-1.600	-1.681	-1.681	73.023	16.145
0.55	11.594	9.486	29.651	-1.449	-1.771	-1.480	-1.809	73.219	15.929
0.60	11.925	7.950	29.718	-1.309	-1.963	-1.290	-1.935	73.387	15.702
0.65	12.216	6.578	29.665	-1.176	-2.184	-1.110	-2.062	73.537	15.451
0.70	12.473	5.346	29.489	-1.047	-2.442	-0.938	-2.190	73.674	15.167
0.75	12.699	4.233	29.181	-0.917	-2.750	-0.773	-2.319	73.792	14.856
0.80	12.900	3.225	28.743	-0.781	-3.123	-0.613	-2.452	73.883	14.541
0.85	13.079	2.308	28.182	-0.633	-3.586	-0.457	-2.588	73.940	14.277
0.90	13.240	1.471	27.525	-0.464	-4.175	-0.303	-2.729	73.958	14.159
0.95	13.387	0.705	26.822	-0.260	-4.945	-0.151	-2.875	73.946	14.335
1.00	13.526	-0.000	26.155	0.000	-5.989	0.000	-3.028	73.931	15.019

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-20
Direct Correlation Function Integral Database
n-Propanol(1) / Water(2)
T: 30° C

Pure Component Volumes

V_1^o : 74.9401

V_2^o : 18.1292

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -2.5619

υ_1 : -0.5190

υ_2 : -0.08921

υ_3 : -1.2863

υ_4 : -3.2981

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : 475.0914	g_{12} : 535.0111
λ_{21} : 1442.0742	g_{21} : 1318.2304
	α : 0.4363

This Study, Eq. 5-39

a : -0.007789

b : -0.006157

x_1	$(1\text{-}C_{11})$	$(1\text{-}C_{12})$	$(1\text{-}C_{22})$	$(1\text{-}C_{11})^{ID}$	$(1\text{-}C_{12})^{ID}$	$(1\text{-}C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	193.489	56.812	15.330	261.945	63.369	15.330	-261.38	-0.383
0.05	229.545	61.721	15.633	194.419	47.033	11.378	-221.05	-0.452
0.10	234.462	60.211	14.622	154.573	37.394	9.046	-197.15	-0.507
0.15	223.643	56.000	13.212	128.281	31.033	7.507	-181.23	-0.552
0.20	206.815	51.134	11.819	109.634	26.522	6.416	-170.31	-0.587
0.25	188.934	46.467	10.566	95.719	23.156	5.602	-162.86	-0.614
0.30	172.050	42.239	9.452	84.939	20.548	4.971	-157.90	-0.633
0.35	156.739	38.435	8.438	76.341	18.468	4.468	-154.70	-0.646
0.40	142.930	34.962	7.484	69.324	16.771	4.057	-152.73	-0.655
0.45	130.340	31.735	6.564	63.488	15.359	3.716	-151.57	-0.660
0.50	118.677	28.703	5.670	58.559	14.166	3.427	-150.91	-0.663
0.55	107.727	25.849	4.805	54.340	13.146	3.180	-150.55	-0.664
0.60	97.376	23.183	3.976	50.688	12.262	2.966	-150.35	-0.665
0.65	87.592	20.722	3.187	47.495	11.490	2.780	-150.25	-0.666
0.70	78.390	18.471	2.436	44.682	10.809	2.615	-150.24	-0.666
0.75	69.797	16.412	1.705	42.183	10.205	2.469	-150.33	-0.665
0.80	61.804	14.495	0.965	39.948	9.664	2.338	-150.46	-0.665
0.85	54.342	12.632	0.168	37.939	9.178	2.220	-150.46	-0.665
0.90	47.245	10.707	-0.745	36.122	8.738	2.114	-149.82	-0.667
0.95	40.245	8.583	-1.834	34.471	8.339	2.017	-147.50	-0.678
1.00	32.964	6.152	-3.142	32.964	7.975	1.929	-141.40	-0.707

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-20 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$ NRTL	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	55.160	15.330	-17.05	0.000	-12.19	0.000	67.186	18.129
0.05	2.418	45.949	20.546	-10.22	-0.538	-9.394	-0.494	70.553	18.050
0.10	4.281	38.533	25.026	-7.090	-0.788	-7.372	-0.819	72.456	17.901
0.15	5.744	32.548	28.858	-5.338	-0.942	-5.880	-1.038	73.434	17.765
0.20	6.917	27.669	32.199	-4.231	-1.058	-4.758	-1.189	73.875	17.673
0.25	7.879	23.637	35.177	-3.472	-1.157	-3.900	-1.300	74.040	17.626
0.30	8.682	20.259	37.857	-2.920	-1.251	-3.235	-1.386	74.098	17.605
0.35	9.364	17.389	40.253	-2.498	-1.345	-2.710	-1.459	74.140	17.585
0.40	9.948	14.922	42.345	-2.164	-1.443	-2.291	-1.527	74.208	17.543
0.45	10.454	12.777	44.089	-1.891	-1.547	-1.950	-1.595	74.309	17.468
0.50	10.895	10.895	45.438	-1.661	-1.661	-1.668	-1.668	74.429	17.359
0.55	11.281	9.230	46.356	-1.461	-1.786	-1.431	-1.749	74.549	17.227
0.60	11.622	7.748	46.820	-1.284	-1.927	-1.227	-1.841	74.649	17.092
0.65	11.925	6.421	46.826	-1.123	-2.086	-1.048	-1.946	74.718	16.978
0.70	12.195	5.227	46.388	-0.972	-2.267	-0.886	-2.067	74.755	16.903
0.75	12.439	4.146	45.522	-0.826	-2.477	-0.735	-2.206	74.768	16.868
0.80	12.660	3.165	44.232	-0.680	-2.721	-0.591	-2.365	74.776	16.841
0.85	12.862	2.270	42.487	-0.531	-3.010	-0.450	-2.548	74.796	16.741
0.90	13.044	1.449	40.188	-0.373	-3.355	-0.306	-2.756	74.841	16.417
0.95	13.206	0.695	37.132	-0.199	-3.774	-0.158	-2.994	74.902	15.620
1.00	13.344	-0.000	32.964	0.000	-4.290	0.000	-3.266	74.940	13.985

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-21
Direct Correlation Function Integral Database
1,4-Dioxane(1) / Benzene(2)
T: 25° C

Pure Component Volumes

V_1° : 85.6646

V_2° : 89.5022

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.261

υ_1 : -0.247

υ_2 : -0.058

υ_3 : 0.022

υ_4 : 0.018

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : 503.079	g_{12} : -386.1822
λ_{21} : -328.8692	g_{21} : 542.1749
	α : 0.3026

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	32.190	34.570	36.342	33.292	34.784	36.342	-25.243	-3.961
0.05	36.569	38.972	40.892	33.926	35.446	37.034	-23.392	-4.275
0.10	41.010	43.464	45.539	34.585	36.134	37.753	-21.543	-4.642
0.15	45.487	48.014	50.248	35.269	36.849	38.500	-19.719	-5.071
0.20	49.969	52.585	54.979	35.981	37.593	39.277	-17.936	-5.575
0.25	54.412	57.128	59.682	36.723	38.368	40.087	-16.204	-6.171
0.30	58.766	61.589	64.302	37.496	39.175	40.930	-14.532	-6.881
0.35	62.969	65.905	68.772	38.301	40.017	41.810	-12.926	-7.737
0.40	66.953	70.001	73.018	39.143	40.896	42.728	-11.389	-8.781
0.45	70.635	73.793	76.953	40.022	41.815	43.688	-9.926	-10.075
0.50	73.923	77.184	80.474	40.941	42.776	44.692	-8.540	-11.710
0.55	76.710	80.063	83.468	41.904	43.781	45.743	-7.236	-13.820
0.60	78.878	82.303	85.802	42.913	44.836	46.844	-6.017	-16.619
0.65	80.287	83.761	87.325	43.972	45.942	48.000	-4.888	-20.458
0.70	80.783	84.274	87.867	45.085	47.105	49.215	-3.854	-25.949
0.75	80.191	83.657	87.235	46.255	48.327	50.492	-2.920	-34.252
0.80	78.314	81.704	85.213	47.488	49.615	51.838	-2.091	-47.815
0.85	74.932	78.183	81.556	48.788	50.974	53.257	-1.376	-72.675
0.90	69.799	72.837	75.996	50.161	52.408	54.756	-0.781	-128.09
0.95	62.640	65.378	68.230	51.614	53.926	56.342	-0.314	-318.87
1.00	53.154	55.488	57.925	53.154	55.535	58.023	0.017	6016.48

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-21 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	11.173	36.342	-0.695	0.000	-0.480	0.000	85.139	89.502
0.05	0.560	10.640	40.699	-0.546	-0.029	-0.409	-0.022	85.233	89.500
0.10	1.123	10.104	45.120	-0.430	-0.048	-0.346	-0.038	85.320	89.493
0.15	1.688	9.565	49.572	-0.338	-0.060	-0.291	-0.051	85.398	89.482
0.20	2.256	9.023	54.012	-0.266	-0.066	-0.243	-0.061	85.465	89.468
0.25	2.826	8.478	58.395	-0.208	-0.069	-0.201	-0.067	85.521	89.451
0.30	3.399	7.930	62.664	-0.162	-0.070	-0.165	-0.071	85.566	89.434
0.35	3.974	7.380	66.757	-0.126	-0.068	-0.134	-0.072	85.602	89.417
0.40	4.551	6.827	70.600	-0.097	-0.065	-0.107	-0.071	85.629	89.401
0.45	5.131	6.271	74.109	-0.074	-0.060	-0.085	-0.069	85.648	89.387
0.50	5.713	5.713	77.191	-0.055	-0.055	-0.065	-0.065	85.661	89.375
0.55	6.298	5.153	79.738	-0.041	-0.050	-0.049	-0.060	85.669	89.367
0.60	6.885	4.590	81.630	-0.029	-0.044	-0.036	-0.054	85.673	89.361
0.65	7.474	4.025	82.730	-0.021	-0.038	-0.025	-0.047	85.674	89.359
0.70	8.066	3.457	82.887	-0.014	-0.033	-0.017	-0.039	85.674	89.360
0.75	8.661	2.887	81.931	-0.009	-0.027	-0.010	-0.030	85.672	89.365
0.80	9.258	2.315	79.675	-0.005	-0.021	-0.005	-0.021	85.670	89.372
0.85	9.858	1.740	75.910	-0.003	-0.015	-0.002	-0.012	85.668	89.381
0.90	10.460	1.162	70.407	-0.001	-0.010	-0.000	-0.002	85.666	89.394
0.95	11.066	0.582	62.914	-0.000	-0.005	0.000	0.008	85.665	89.408
1.00	11.673	-0.000	53.154	-0.000	0.000	-0.000	0.018	85.665	89.426

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-22
Direct Correlation Function Integral Database
Cyclopentane(1) / Cyclooctane(2)
T: 25° C

Pure Component Volumes

V_1^o : 94.7319

V_2^o :134.8728

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -1.1311

υ_1 : 0.4337

υ_2 : 0.01413

υ_3 : 0.01909

υ_4 : 0.00316

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 557.759

λ_{21} : -492.1817

NRTL, Eq. H-7,8

g_{12} : -238.631

g_{21} : 276.124

α : 0.5

x_1	$(1\text{-}C_{11})$	$(1\text{-}C_{12})$	$(1\text{-}C_{22})$	$(1\text{-}C_{11})^{ID}$	$(1\text{-}C_{12})^{ID}$	$(1\text{-}C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.0000	32.961	47.262	67.761	33.429	47.594	67.761	-0.188	-531.88
0.0509	33.059	47.395	67.975	33.152	47.199	67.199	0.848	117.969
0.1382	33.006	47.301	67.848	32.687	46.538	66.257	2.055	48.652
0.2467	32.997	47.246	67.736	32.127	45.741	65.123	2.872	34.813
0.3446	32.747	46.834	67.078	31.639	45.045	64.132	3.173	31.520
0.4249	32.560	46.510	66.536	31.249	44.490	63.341	3.234	30.920
0.5144	32.316	46.086	65.824	30.825	43.887	62.483	3.174	31.505
0.6081	32.172	45.791	65.270	30.394	43.273	61.609	3.034	32.955
0.6864	31.731	45.078	64.129	30.043	42.773	60.897	2.848	35.110
0.7728	31.105	44.088	62.573	29.664	42.234	60.130	2.612	38.284
0.8436	30.503	43.145	61.104	29.361	41.803	59.516	2.408	41.528
0.9188	29.725	41.944	59.260	29.046	41.354	58.877	2.185	45.759
0.9721	29.156	41.068	57.917	28.827	41.042	58.433	2.032	49.204
1.0000	28.714	40.406	56.926	28.714	40.881	58.203	1.94	51.417

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-22 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.0000	0.000	7.414	67.761	-0.003	0.000	0.028	0.000	94.071	134.87
0.0509	0.383	7.147	65.896	0.012	0.001	0.032	0.002	94.041	134.87
0.1382	1.069	6.669	62.288	0.028	0.005	0.037	0.006	94.036	134.87
0.2467	1.977	6.036	58.006	0.037	0.012	0.039	0.013	94.088	134.86
0.3446	2.852	5.425	53.857	0.039	0.020	0.038	0.020	94.172	134.82
0.4249	3.614	4.892	50.615	0.037	0.027	0.035	0.026	94.256	134.77
0.5144	4.515	4.262	47.097	0.033	0.035	0.032	0.033	94.357	134.68
0.6081	5.520	3.557	43.747	0.027	0.042	0.027	0.041	94.464	134.54
0.6864	6.412	2.930	40.663	0.022	0.048	0.022	0.048	94.547	134.39
0.7728	7.459	2.193	37.288	0.016	0.054	0.016	0.055	94.627	134.17
0.8436	8.367	1.551	34.587	0.011	0.059	0.011	0.061	94.679	133.95
0.9188	9.387	0.830	31.743	0.006	0.063	0.006	0.067	94.717	133.67
0.9721	10.146	0.291	29.825	0.002	0.066	0.002	0.072	94.730	133.44
1.0000	10.556	0.000	28.714	0.000	0.068	0.000	0.074	94.732	133.31

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-23
Direct Correlation Function Integral Database
Cyclopentane(1) / OMCTS(2)
T: 25° C

Pure Component Volumes

V_1^o : 94.71

V_2^o :312.12

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 0.1841

υ_1 : 0.064

υ_2 : -0.140

υ_3 : 0.168

υ_4 : -0.106

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 128.08

λ_{21} : -17.53

NRTL, Eq. H-7,8

g_{12} : -655.83

g_{21} : 1129.13

α : 0.5

This Study, Eq. 5-39

a : 0.03376

b : -0.01391

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.0000	7.945	25.002	82.246	7.573	24.957	82.246	28.321	3.531
0.0805	8.408	26.578	87.531	8.050	26.529	87.428	29.535	3.386
0.1584	8.917	28.314	93.365	8.573	28.251	93.103	30.814	3.245
0.2942	9.962	31.878	105.340	9.667	31.857	104.985	33.199	3.012
0.3969	10.969	35.301	116.815	10.699	35.260	116.199	35.262	2.836
0.5153	12.453	40.328	133.650	12.202	40.212	132.519	37.916	2.637
0.6296	14.331	46.678	154.872	14.116	46.519	153.305	40.648	2.460
0.7091	16.058	52.492	174.253	15.844	52.215	172.077	42.686	2.343
0.7601	17.387	56.957	189.102	17.195	56.667	186.747	43.928	2.276
0.7676	17.616	57.723	191.645	17.413	57.386	189.118	44.142	2.265
0.8101	18.928	62.112	206.206	18.763	61.835	203.779	45.078	2.218
0.8597	20.777	68.281	226.612	20.630	67.986	224.049	46.137	2.167
0.8963	22.405	73.690	244.460	22.264	73.371	241.798	46.809	2.136
0.9331	24.287	79.931	265.000	24.191	79.721	262.723	47.247	2.117
0.9563	25.687	84.559	280.204	25.587	84.321	277.884	47.47	2.107
0.9771	27.051	89.061	294.971	26.983	88.922	293.046	47.50	2.105
0.9884	27.859	91.722	303.691	27.807	91.638	301.997	47.47	2.107
1.00	28.707	94.516	312.836	28.707	94.605	311.774	47.34	2.112

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-23 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.0000	0.000	3.204	82.246	0.344	0.000	-3.188	0.000	94.880	312.12
0.0805	0.273	3.121	77.995	0.348	0.030	-1.151	-0.101	94.876	312.12
0.1584	0.570	3.031	73.903	0.351	0.066	-0.192	-0.036	94.853	312.12
0.2942	1.185	2.844	66.577	0.352	0.147	0.417	0.174	94.806	312.14
0.3969	1.757	2.670	61.117	0.348	0.229	0.496	0.327	94.773	312.15
0.5153	2.575	2.422	54.851	0.335	0.356	0.439	0.467	94.735	312.19
0.6296	3.592	2.113	48.699	0.309	0.526	0.333	0.566	94.701	312.23
0.7091	4.489	1.841	44.476	0.279	0.681	0.253	0.616	94.684	312.27
0.7601	5.175	1.633	41.701	0.253	0.801	0.202	0.641	94.679	312.28
0.7676	5.285	1.600	41.325	0.248	0.820	0.195	0.644	94.679	312.28
0.8101	5.957	1.396	38.968	0.220	0.937	0.155	0.661	94.680	312.28
0.8597	6.866	1.121	36.288	0.178	1.093	0.111	0.677	94.686	312.24
0.8963	7.644	0.884	34.326	0.141	1.222	0.080	0.687	94.693	312.19
0.9331	8.541	0.612	32.312	0.098	1.364	0.050	0.695	94.701	312.11
0.9563	9.177	0.419	31.094	0.067	1.460	0.032	0.700	94.706	312.03
0.9771	9.802	0.230	29.967	0.036	1.549	0.016	0.703	94.709	311.94
0.9884	10.166	0.119	29.360	0.019	1.598	0.008	0.705	94.710	311.89
1.0000	10.559	0.000	28.707	0.000	1.649	0.000	0.706	94.710	311.83

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-24
Direct Correlation Function Integral Database
Pyridine(1) / Benzene(2)
T: 25° C

Pure Component Volumes

V_1^o : 80.8341

V_2^o : 89.5022

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.799

υ_1 : -0.144

υ_2 : 0.0

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 116.3473

λ_{21} : 32.8427

NRTL, Eq. H-7,8

g_{12} : 68.3481

g_{21} : 79.4851

α : 0.3022

This Study, Eq. 5-39

a : -0.05772

b : 0.01879

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	28.488	32.440	36.342	29.644	32.822	36.342	-17.015	-5.877
0.05	29.516	33.513	37.462	30.245	33.488	37.079	-17.408	-5.745
0.10	30.553	34.596	38.592	30.871	34.182	37.847	-17.805	-5.616
0.15	31.598	35.687	39.730	31.524	34.904	38.647	-18.208	-5.492
0.20	32.650	36.786	40.875	32.205	35.658	39.482	-18.614	-5.372
0.25	33.708	37.890	42.027	32.916	36.446	40.354	-19.024	-5.256
0.30	34.771	38.999	43.183	33.659	37.268	41.265	-19.438	-5.145
0.35	35.836	40.112	44.343	34.436	38.129	42.218	-19.855	-5.037
0.40	36.904	41.226	45.504	35.251	39.031	43.216	-20.274	-4.933
0.45	37.971	42.340	46.666	36.104	39.976	44.262	-20.695	-4.832
0.50	39.037	43.453	47.827	37.000	40.968	45.361	-21.117	-4.736
0.55	40.100	44.563	48.985	37.942	42.010	46.515	-21.540	-4.643
0.60	41.159	45.668	50.138	38.932	43.107	47.730	-21.963	-4.553
0.65	42.211	46.767	51.285	39.976	44.263	49.010	-22.385	-4.467
0.70	43.254	47.858	52.423	41.078	45.483	50.360	-22.806	-4.385
0.75	44.287	48.937	53.551	42.242	46.771	51.787	-23.225	-4.306
0.80	45.308	50.004	54.666	43.473	48.135	53.297	-23.640	-4.230
0.85	46.313	51.056	55.765	44.779	49.581	54.897	-24.051	-4.158
0.90	47.301	52.089	56.846	46.165	51.116	56.597	-24.456	-4.089
0.95	48.269	53.102	57.905	47.641	52.749	58.406	-24.854	-4.023
1.00	49.213	54.092	58.941	49.213	54.490	60.333	-25.244	-3.961

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-24 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	11.173	36.342	-0.468	0.000	-0.495	0.000	79.891	89.502
0.05	0.562	10.671	37.067	-0.446	-0.023	-0.469	-0.025	80.009	89.499
0.10	1.129	10.163	37.792	-0.424	-0.047	-0.444	-0.049	80.117	89.490
0.15	1.703	9.650	38.516	-0.402	-0.071	-0.419	-0.074	80.215	89.476
0.20	2.282	9.130	39.238	-0.380	-0.095	-0.394	-0.098	80.304	89.458
0.25	2.868	8.604	39.956	-0.357	-0.119	-0.369	-0.123	80.385	89.434
0.30	3.459	8.072	40.669	-0.335	-0.143	-0.344	-0.147	80.457	89.407
0.35	4.057	7.534	41.376	-0.312	-0.168	-0.319	-0.172	80.521	89.376
0.40	4.660	6.990	42.074	-0.289	-0.193	-0.294	-0.196	80.578	89.342
0.45	5.269	6.440	42.764	-0.266	-0.218	-0.269	-0.220	80.627	89.305
0.50	5.885	5.885	43.443	-0.243	-0.243	-0.245	-0.245	80.670	89.266
0.55	6.506	5.323	44.109	-0.220	-0.269	-0.220	-0.269	80.707	89.226
0.60	7.133	4.755	44.760	-0.196	-0.294	-0.195	-0.293	80.739	89.183
0.65	7.766	4.182	45.396	-0.173	-0.321	-0.171	-0.317	80.764	89.140
0.70	8.405	3.602	46.013	-0.149	-0.347	-0.146	-0.342	80.786	89.097
0.75	9.051	3.017	46.610	-0.125	-0.374	-0.122	-0.366	80.802	89.053
0.80	9.702	2.426	47.185	-0.100	-0.401	-0.097	-0.390	80.815	89.009
0.85	10.360	1.828	47.735	-0.076	-0.428	-0.073	-0.414	80.824	88.967
0.90	11.024	1.225	48.258	-0.051	-0.456	-0.049	-0.438	80.830	88.925
0.95	11.694	0.615	48.752	-0.025	-0.484	-0.024	-0.462	80.833	88.885
1.00	12.371	-0.000	49.213	0.000	-0.513	0.000	-0.486	80.834	88.847

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-25
Direct Correlation Function Integral Database
Chlorobenzene(1) / Aniline(2)
T: 25° C

Pure Component Volumes

V_1^o :102.2604

V_2^o : 91.6073

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 0.4674

υ_1 : -0.0684

υ_2 : 0.0121

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : -34.2767

λ_{21} : 433.3115

NRTL, Eq. H-7,8

g_{12} : 471.6784

g_{21} : -74.1166

α : 0.3006

This Study, Eq. 5-39

a : -0.01597

b : 0.005673

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	98.552	88.662	79.107	98.576	88.307	79.107	-64.750	-1.544
0.05	95.526	85.977	76.698	94.821	84.943	76.094	-65.281	-1.532
0.10	92.612	83.389	74.372	91.342	81.827	73.302	-65.880	-1.518
0.15	89.804	80.894	72.126	88.110	78.931	70.708	-66.553	-1.503
0.20	87.100	78.489	69.956	85.098	76.233	68.291	-67.306	-1.486
0.25	84.494	76.170	67.860	82.285	73.713	66.034	-68.146	-1.467
0.30	81.984	73.934	65.833	79.653	71.355	63.921	-69.080	-1.448
0.35	79.565	71.779	63.873	77.183	69.143	61.940	-70.116	-1.426
0.40	77.235	69.700	61.977	74.862	67.063	60.077	-71.266	-1.403
0.45	74.990	67.695	60.141	72.677	65.106	58.323	-72.539	-1.379
0.50	72.827	65.760	58.362	70.615	63.259	56.669	-73.949	-1.352
0.55	70.743	63.892	56.637	68.668	61.514	55.106	-75.509	-1.324
0.60	68.734	62.088	54.962	66.825	59.863	53.627	-77.236	-1.295
0.65	66.797	60.346	53.333	65.078	58.298	52.225	-79.150	-1.263
0.70	64.929	58.661	51.746	63.420	56.813	50.895	-81.273	-1.230
0.75	63.128	57.031	50.197	61.845	55.402	49.630	-83.631	-1.196
0.80	61.391	55.452	48.683	60.345	54.059	48.427	-86.254	-1.159
0.85	59.713	53.921	47.197	58.917	52.780	47.281	-89.179	-1.121
0.90	58.093	52.434	45.735	57.555	51.559	46.188	-92.449	-1.082
0.95	56.527	50.987	44.290	56.255	50.394	45.144	-96.115	-1.040
1.00	55.012	49.576	42.854	55.012	49.281	44.147	-100.24	-0.998

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-25 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
				Wilson		NRTL			
0.00	0.000	10.916	79.107	-0.819	0.000	-0.745	0.000	102.67	91.607
0.05	0.543	10.308	77.627	-0.799	-0.042	-0.737	-0.039	102.64	91.608
0.10	1.079	9.708	76.178	-0.778	-0.086	-0.728	-0.081	102.61	91.611
0.15	1.608	9.114	74.760	-0.757	-0.134	-0.716	-0.126	102.58	91.615
0.20	2.132	8.528	73.372	-0.734	-0.183	-0.702	-0.176	102.55	91.621
0.25	2.650	7.949	72.016	-0.710	-0.237	-0.686	-0.229	102.52	91.629
0.30	3.161	7.376	70.689	-0.684	-0.293	-0.667	-0.286	102.49	91.640
0.35	3.667	6.811	69.393	-0.657	-0.354	-0.646	-0.348	102.47	91.652
0.40	4.168	6.251	68.125	-0.628	-0.418	-0.622	-0.415	102.44	91.668
0.45	4.662	5.699	66.887	-0.596	-0.488	-0.594	-0.486	102.42	91.686
0.50	5.152	5.152	65.677	-0.563	-0.563	-0.564	-0.564	102.39	91.707
0.55	5.636	4.611	64.495	-0.527	-0.644	-0.530	-0.647	102.37	91.732
0.60	6.115	4.077	63.340	-0.488	-0.732	-0.491	-0.737	102.35	91.760
0.65	6.589	3.548	62.212	-0.445	-0.827	-0.449	-0.834	102.33	91.792
0.70	7.059	3.025	61.110	-0.399	-0.931	-0.402	-0.938	102.31	91.828
0.75	7.523	2.508	60.034	-0.348	-1.045	-0.350	-1.050	102.30	91.869
0.80	7.983	1.996	58.982	-0.292	-1.170	-0.293	-1.171	102.29	91.914
0.85	8.438	1.489	57.955	-0.231	-1.308	-0.230	-1.301	102.28	91.965
0.90	8.890	0.988	56.951	-0.162	-1.461	-0.160	-1.440	102.27	92.022
0.95	9.336	0.491	55.970	-0.086	-1.631	-0.084	-1.591	102.26	92.085
1.00	9.779	-0.000	55.012	0.000	-1.822	0.000	-1.753	102.26	92.155

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-26
Direct Correlation Function Integral Database
Nitrobenzene(1) / Aniline(2)
T: 60° C

Pure Component Volumes

V_1^o :105.7746

V_2^o : 94.2524

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : 1.218

υ_1 : 0.1295

υ_2 : 0.04491f0

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†	NRTL, Eq. H-7,8
λ_{12} : -244.7227	g_{12} : 393.6259
λ_{21} : 353.9286	g_{21} : -273.6049
	α : 0.2906

This Study, Eq. 5-39

a : -0.1294

b : 0.09044

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	75.202	66.244	58.261	73.376	65.383	58.261	-6.906	-14.480
0.05	73.939	65.243	57.471	72.660	64.745	57.692	-7.266	-13.762
0.10	72.762	64.309	56.733	71.958	64.119	57.135	-7.652	-13.069
0.15	71.664	63.438	56.044	71.269	63.505	56.588	-8.065	-12.399
0.20	70.639	62.625	55.399	70.593	62.903	56.051	-8.508	-11.753
0.25	69.683	61.866	54.796	69.930	62.312	55.525	-8.984	-11.131
0.30	68.791	61.157	54.233	69.279	61.733	55.008	-9.496	-10.531
0.35	67.959	60.497	53.706	68.641	61.163	54.501	-10.046	-9.954
0.40	67.182	59.881	53.215	68.013	60.605	54.003	-10.639	-9.399
0.45	66.459	59.307	52.755	67.398	60.056	53.514	-11.279	-8.866
0.50	65.785	58.773	52.327	66.793	59.517	53.034	-11.971	-8.354
0.55	65.157	58.277	51.928	66.199	58.988	52.562	-12.718	-7.863
0.60	64.575	57.817	51.558	65.616	58.468	52.099	-13.528	-7.392
0.65	64.034	57.392	51.213	65.042	57.957	51.644	-14.406	-6.941
0.70	63.534	56.999	50.895	64.479	57.455	51.197	-15.361	-6.510
0.75	63.072	56.638	50.601	63.925	56.962	50.757	-16.399	-6.098
0.80	62.647	56.308	50.330	63.381	56.477	50.325	-17.529	-5.705
0.85	62.258	56.007	50.082	62.846	56.000	49.900	-18.764	-5.329
0.90	61.903	55.735	49.856	62.320	55.531	49.482	-20.113	-4.972
0.95	61.582	55.491	49.651	61.803	55.070	49.071	-21.592	-4.631
1.00	61.294	55.274	49.466	61.294	54.617	48.667	-23.214	-4.308

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-26 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	10.610	58.261	-0.119	0.000	-0.109	0.000	107.17	94.252
0.05	0.527	10.011	58.251	-0.119	-0.006	-0.111	-0.006	106.99	94.257
0.10	1.047	9.422	58.257	-0.118	-0.013	-0.112	-0.012	106.84	94.270
0.15	1.560	8.840	58.281	-0.118	-0.021	-0.113	-0.020	106.69	94.290
0.20	2.067	8.267	58.321	-0.117	-0.029	-0.114	-0.028	106.57	94.317
0.25	2.567	7.702	58.378	-0.115	-0.038	-0.114	-0.038	106.45	94.350
0.30	3.062	7.145	58.451	-0.114	-0.049	-0.113	-0.048	106.35	94.388
0.35	3.551	6.594	58.542	-0.112	-0.060	-0.112	-0.060	106.26	94.432
0.40	4.034	6.051	58.649	-0.109	-0.073	-0.109	-0.073	106.18	94.480
0.45	4.512	5.514	58.773	-0.106	-0.086	-0.107	-0.087	106.11	94.533
0.50	4.984	4.984	58.915	-0.102	-0.102	-0.103	-0.103	106.05	94.589
0.55	5.452	4.460	59.073	-0.097	-0.118	-0.098	-0.120	105.99	94.650
0.60	5.914	3.943	59.248	-0.091	-0.137	-0.092	-0.139	105.94	94.714
0.65	6.372	3.431	59.441	-0.085	-0.158	-0.086	-0.159	105.90	94.783
0.70	6.825	2.925	59.652	-0.077	-0.180	-0.078	-0.182	105.87	94.855
0.75	7.274	2.425	59.880	-0.068	-0.205	-0.069	-0.206	105.84	94.931
0.80	7.718	1.929	60.126	-0.058	-0.233	-0.058	-0.232	105.82	95.012
0.85	8.158	1.440	60.390	-0.047	-0.264	-0.046	-0.261	105.80	95.097
0.90	8.594	0.955	60.672	-0.033	-0.298	-0.032	-0.292	105.78	95.188
0.95	9.026	0.475	60.974	-0.018	-0.336	-0.017	-0.326	105.78	95.284
1.00	9.454	-0.000	61.294	0.000	-0.379	0.000	-0.362	105.77	95.386

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-27
Direct Correlation Function Integral Database
Benzene(1) / Aniline(2)
T: 25° C

Pure Component Volumes

V_1^o : 89.5022

V_2^o : 91.6073

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -1.1049

υ_1 : -0.4876

υ_2 : 0.6536

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†		NRTL, Eq. H-7,8	
λ_{12} :	18.0376	g_{12} :	704.0784
λ_{21} :	535.1142	g_{21} :	-150.335
		α :	0.3001

This Study, Eq. 5-39

a : -0.01561

b : 0.006420f0

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	72.879	76.271	78.893	75.309	77.080	78.893	-67.665	-1.478
0.05	70.785	74.125	76.661	71.677	73.363	75.088	-68.125	-1.468
0.10	68.747	71.990	74.388	68.380	69.988	71.634	-68.597	-1.458
0.15	66.754	69.862	72.080	65.372	66.910	68.484	-69.102	-1.447
0.20	64.795	67.742	69.748	62.618	64.091	65.599	-69.660	-1.436
0.25	62.865	65.631	67.400	60.087	61.500	62.947	-70.291	-1.423
0.30	60.958	63.531	65.048	57.752	59.111	60.501	-71.019	-1.408
0.35	59.071	61.447	62.702	55.592	56.900	58.238	-71.866	-1.391
0.40	57.205	59.384	60.373	53.588	54.849	56.139	-72.860	-1.372
0.45	55.359	57.348	58.070	51.724	52.940	54.185	-74.028	-1.351
0.50	53.536	55.344	55.804	49.984	51.160	52.363	-75.403	-1.326
0.55	51.738	53.378	53.582	48.358	49.495	50.660	-77.021	-1.298
0.60	49.968	51.458	51.412	46.834	47.936	49.063	-78.928	-1.267
0.65	48.232	49.589	49.300	45.404	46.472	47.565	-81.175	-1.232
0.70	46.534	47.776	47.250	44.058	45.094	46.155	-83.826	-1.193
0.75	44.879	46.026	45.264	42.790	43.796	44.826	-86.960	-1.150
0.80	43.271	44.341	43.342	41.592	42.571	43.572	-90.678	-1.103
0.85	41.716	42.726	41.481	40.460	41.412	42.386	-95.109	-1.051
0.90	40.218	41.182	39.672	39.388	40.314	41.263	-100.42	-0.996
0.95	38.780	39.708	37.903	38.371	39.274	40.197	-106.84	-0.936
1.00	37.406	38.301	36.151	37.406	38.285	39.186	-114.67	-0.872

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-27 Continued

x_1	ρ_1 x 10^3 gmol/cc	ρ_2 x 10^3 gmol/cc	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\dagger}$ Wilson	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\dagger}$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^{\ddagger}$ NRTL	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^{\ddagger}$	$\overline{V}_1$ cc/gmol	$\overline{V}_2$ cc/gmol
0.00	0.000	10.916	78.893	-0.858	0.000	-0.694	-0.000	88.563	91.607
0.05	0.547	10.388	76.406	-0.847	-0.045	-0.706	-0.037	88.525	91.608
0.10	1.095	9.858	73.900	-0.835	-0.093	-0.716	-0.080	88.540	91.607
0.15	1.646	9.325	71.395	-0.823	-0.145	-0.723	-0.128	88.596	91.598
0.20	2.198	8.791	68.908	-0.809	-0.202	-0.729	-0.182	88.682	91.580
0.25	2.752	8.255	66.453	-0.793	-0.264	-0.731	-0.244	88.789	91.549
0.30	3.307	7.716	64.043	-0.776	-0.333	-0.730	-0.313	88.906	91.504
0.35	3.863	7.174	61.687	-0.757	-0.408	-0.726	-0.391	89.027	91.446
0.40	4.421	6.631	59.392	-0.736	-0.491	-0.717	-0.478	89.144	91.376
0.45	4.979	6.086	57.164	-0.712	-0.583	-0.704	-0.576	89.252	91.296
0.50	5.538	5.538	55.007	-0.685	-0.685	-0.685	-0.685	89.348	91.209
0.55	6.098	4.989	52.923	-0.655	-0.800	-0.661	-0.808	89.427	91.121
0.60	6.659	4.439	50.914	-0.620	-0.930	-0.630	-0.944	89.489	91.038
0.65	7.219	3.887	48.980	-0.580	-1.077	-0.591	-1.097	89.532	90.967
0.70	7.781	3.335	47.120	-0.534	-1.245	-0.543	-1.268	89.557	90.916
0.75	8.343	2.781	45.333	-0.480	-1.439	-0.486	-1.459	89.566	90.894
0.80	8.906	2.226	43.616	-0.416	-1.663	-0.418	-1.672	89.561	90.912
0.85	9.470	1.671	41.968	-0.340	-1.926	-0.337	-1.909	89.546	90.983
0.90	10.035	1.115	40.386	-0.249	-2.238	-0.242	-2.175	89.527	91.119
0.95	10.603	0.558	38.866	-0.137	-2.611	-0.130	-2.472	89.510	91.334
1.00	11.173	-0.000	37.406	0.000	-3.066	0.000	-2.805	89.502	91.644

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

Table H-28
Direct Correlation Function Integral Database
Aniline(1) / Toluene(2)
T: 20° C

Pure Component Volumes

V_1^o : 91.2483

V_2^o :105.9872

Excess Volume Parameters

Eq. D-1, D-3 and D-4

υ_0 : -0.589

υ_1 : 0.2713

υ_2 : 0.0

υ_3 : 0.0

υ_4 : 0.0

Activity Coefficient Parameters

Wilson, Eq. H-3,4†

λ_{12} : 874.8649

λ_{21} : 659.3165

NRTL, Eq. H-7,8

g_{12} : 844.9388

g_{21} : 950.5085

α : 0.6125

This Study, Eq. 5-39

a : -0.04885

b : 0.001675

x_1	$(1-C_{11})$	$(1-C_{12})$	$(1-C_{22})$	$(1-C_{11})^{ID}$	$(1-C_{12})^{ID}$	$(1-C_{22})^{ID}$	ΔC	$1/\Delta C$ x 10^2
0.00	30.322	43.100	50.236	37.236	43.250	50.236	-334.31	-0.299
0.05	33.198	44.932	52.055	38.279	44.462	51.644	-290.77	-0.344
0.10	35.706	46.773	53.964	39.382	45.744	53.132	-260.89	-0.383
0.15	38.016	48.660	55.972	40.551	47.101	54.709	-239.97	-0.417
0.20	40.228	50.615	58.084	41.792	48.542	56.383	-225.31	-0.444
0.25	42.401	52.651	60.303	43.110	50.074	58.162	-215.27	-0.465
0.30	44.577	54.779	62.630	44.515	51.705	60.057	-208.83	-0.479
0.35	46.781	57.002	65.067	46.014	53.446	62.079	-205.35	-0.487
0.40	49.033	59.326	67.611	47.618	55.309	64.243	-204.43	-0.489
0.45	51.346	61.753	70.261	49.337	57.306	66.563	-205.88	-0.486
0.50	53.729	64.284	73.012	51.185	59.453	69.056	-209.64	-0.477
0.55	56.188	66.919	75.858	53.178	61.767	71.744	-215.77	-0.463
0.60	58.728	69.655	78.791	55.331	64.268	74.649	-224.47	-0.445
0.65	61.352	72.489	81.800	57.666	66.981	77.800	-236.09	-0.424
0.70	64.058	75.417	84.870	60.208	69.933	81.228	-251.18	-0.398
0.75	66.848	78.432	87.978	62.983	73.156	84.973	-270.53	-0.370
0.80	69.716	81.524	91.096	66.027	76.692	89.079	-295.32	-0.339
0.85	72.659	84.679	94.183	69.379	80.586	93.603	-327.31	-0.306
0.90	75.670	87.880	97.182	73.091	84.897	98.610	-369.18	-0.271
0.95	78.738	91.099	100.001	77.222	89.695	104.183	-425.19	-0.235
1.00	81.848	94.297	102.501	81.848	95.069	110.425	-502.39	-0.199

† The Wilson activity coefficient parameters were used in generation of this table.

Table H-28 Continued

x_1	ρ_1 x 10^3	ρ_2 x 10^3	χ	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\dagger$	$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)^\ddagger$	$\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)^\ddagger$	$\overline{V}_1$	$\overline{V}_2$
	gmol/cc	gmol/cc		Wilson		NRTL		cc/gmol	cc/gmol
0.00	0.000	9.435	50.236	-6.655	0.000	-9.358	0.000	90.931	105.99
0.05	0.475	9.028	51.331	-5.381	-0.283	-7.089	-0.373	90.913	105.99
0.10	0.957	8.614	52.487	-4.473	-0.497	-5.491	-0.610	90.903	105.99
0.15	1.446	8.195	53.703	-3.798	-0.670	-4.340	-0.766	90.901	105.99
0.20	1.942	7.769	54.980	-3.279	-0.820	-3.498	-0.874	90.906	105.99
0.25	2.446	7.337	56.315	-2.867	-0.956	-2.871	-0.957	90.917	105.98
0.30	2.957	6.899	57.708	-2.533	-1.086	-2.400	-1.029	90.933	105.98
0.35	3.475	6.454	59.157	-2.256	-1.215	-2.042	-1.100	90.954	105.97
0.40	4.001	6.002	60.662	-2.022	-1.348	-1.768	-1.178	90.978	105.95
0.45	4.536	5.543	62.219	-1.820	-1.489	-1.555	-1.272	91.004	105.93
0.50	5.078	5.078	63.827	-1.642	-1.642	-1.389	-1.389	91.033	105.91
0.55	5.628	4.605	65.483	-1.483	-1.812	-1.257	-1.536	91.063	105.87
0.60	6.186	4.124	67.183	-1.336	-2.005	-1.149	-1.724	91.093	105.83
0.65	6.753	3.636	68.924	-1.199	-2.227	-1.058	-1.964	91.123	105.78
0.70	7.328	3.141	70.702	-1.066	-2.487	-0.974	-2.272	91.151	105.73
0.75	7.912	2.637	72.513	-0.933	-2.798	-0.890	-2.669	91.178	105.66
0.80	8.504	2.126	74.350	-0.794	-3.178	-0.796	-3.182	91.201	105.58
0.85	9.105	1.607	76.209	-0.644	-3.651	-0.680	-3.852	91.220	105.48
0.90	9.714	1.079	78.083	-0.473	-4.255	-0.526	-4.734	91.235	105.38
0.95	10.332	0.544	79.965	-0.266	-5.051	-0.311	-5.909	91.245	105.26
1.00	10.959	-0.000	81.848	0.000	-6.138	0.000	-7.496	91.248	105.13

† Calculated using the Wilson activity coefficient model, Eq. H-3,4.

‡ Calculated using the NRTL activity coefficient model, Eq. H-7,8.

APPENDIX I

FORTRAN PROGRAMS FOR REGRESSION OF ACTIVITY COEFFICIENT DATA TO EQUATIONS 5-39a AND 5-39b

The FORTRAN program LNGM was written to regress activity coefficient data to the model developed in this study (equations 5-39a and 5-39b). The generalized least squares method described in Appendix G was used. The primary difference with this system is that there are two constraint equations (5-39a and 5-39b). The model, WCACM, can be easily adapted to regress data of the form of pressure, temperaure and composition, the usual form for VLE data.

Listing of Computer File LNGM.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
c  this program will regress activity coefficient data to Eq 5-39
c  using generalized least squares
c
c  input data file:
c  line 1: description of data
c  line 2: number of data points
c  line 3: x1,ln(gm1),ln(gm2),std dev x1,std dev ln(gm1),std dev ln(gm2)
c  line n: continue with data in format of line 3
c
c  input parameters file:
c  line 1: volume, component 1, cc/gmole
c  line 2: isothermal compressibility, component 1, 1/bars
c  line 3: volume, component 2, cc/gmole
c  line 4: isothermal compressibility, component 2, 1/bars
c  line 5: temperature, k
c
c$large
      implicit real*8(a-h,o-z)
      dimension param(2),var(6),obs(3,50),cor(3,50),err(3,50),
     >          sumerr(3),avgerr(3)
      external wcacm
      character*1 ans, flnm*40, descrp*80, outfil*40, date*8, time*8
      character a
10    call cls
      call c22p3v(kit,obs,cor,err,param,var,descrp,flnm,wcacm)
c  n  = # Parameters
c  iy = # Variables, x, lngm1, lngm2
20    n = 2
30    iy = 3
      call cls
      write(*,35)
35    format(/,/,20x,'regression results ln(gamma1)',/,
     >           21x,'parameters a, b',10x,'errors',/)
      do 40 i = 1,n
         j = i*(i+1)/2
40    write(*,50)param(i),var(j)
50    format(' ',23x,f15.7,' +/- ',f15.7)
      pause ' '
      call cls
      write(*,60)
60    format(' output residuals to a file, <n>? ',\)
```

Listing of Computer File LNGM.FOR

```
      read(*,'(a)')ans
      if(ans .eq. 'y') goto 65
      goto 999
c
c  call flout to ask for output file name
c  this subroutine is contained within gen.for
c
65    call outfl(flnm,outfil,'dtl')
      open(2,file=outfil,status='new')
      call datev(date,time)
      write(2,'('' '',a8,''  '',a8)')time,date
      write(2,36)descrp
      do 100 i = 1,n
        j = i*(i+1)/2
        sumerr(i) = 0.0
100     write(2,50)param(i),var(j)
        write(2,98)
      do 80 i = 1,kit
          write(2,95)(obs(j,i),cor(j,i),err(j,i),j=1,3)
        do 110 ik = 1,iy
          sumerr(ik) = sumerr(ik) + dabs(err(ik,i))
110     continue
80    continue
99    write(2,'(/)')
      do 120 ik = 1,iy
        avgerr(ik) = sumerr(ik) / i
        write(2,'('' average absolute error variable '',i1,'' = '',
     >  g12.5,1x)')ik,avgerr(ik)
        write(*,'('' average absolute error variable '',i1,'' = '',
     >  g12.5,1x)')ik,avgerr(ik)
120   continue
36    format(/,/,a80,/,/,20x,
     >      ' regression results ln(gamma1)',/,
     >       21x,' parameter  a, b    ',10x,'error',/)
95    format(9g12.5)
98    format(' ',/, ' measured x  estimate x    adjust x measd lngm1    e
     >st lngm1  adj lngm1  meas lngm2  est lngm2   adj  lngm2',
     >/,/)
      close(2)
999   write(*,'('' continue? <n> '',\)')
      read(*,'(a)')ans
      if (ans .eq. 'y') goto 10
      end
c-----------------------------------------------------------------
      subroutine c22p3v(kit,obs,cor,err,param,var,descrp,flnm,wcacm)
c Activity Coefficient Regression
c 2 parameters
```

Listing of Computer File LNGM.FOR

```
c 2 constraint
c 3 variables
c
c  for comments see appendix g
      implicit real*8 (a-h,o-z)
      common /reals/ss,eps,ssnd,sumsq,sigma
      common /ints/nxn,ncxnc,ith,n,m,l,k,nc,iter,iterz,idem,iods,
     >           kout,ndriv,isv.nfeval,ier,ibound,nic,io
      external wcacm
      character*80 descrp, flnm*40
      integer mv(50), ncv(50), iwork(2)
      real*8 p(2),param(2),zm(3,50),x(1,50),var(6),r(3,50),const(10)
      real*8 z(3,50),f(2,50),delz(3,50),covar(30),lb(2)
      real*8 lm(2,2),c(2,1),d(1),ub(2)
      real*8 w(2,2,50),zwork(3,50),delp(2),fprod(2)
      real*8 fptwfp(3),ft(3),fptwfi(3),ff(2,50)
      real*8 fz(2,3,50),fp(2,2,50),fptw(2,2,50),w1(3,50)
      real*8 fzdz(2,50),scale(500)
      real*8 obs(3,50), cor(3,50), err(3,50)
      n = 2
      nc = 2
      m = 3
      l = 1
      ifixed = 0
      icn = 1
c
c  call to generalized least squares
c
      call genmain(icn,ifixed,mv,ncv,iwork,p,zm,x, r,const,
     >z,f,delz,covar,lb,lm,c,d,ub,w,zwork,
     >delp,fprod,fptwfp,ft,fptwfi,ff,fz,fp,fptw,w1,fzdz,scale,
     >descrp,flnm,wcacm)
      kit = k
      do 1000 i = 1,n
1000  param(i) = p(i)
      nxn = n*(n+1)/2
      do 2000 i = 1,nxn
2000  var(i) = ft(i)
      do 3000 i = 1,m
         do 3000 j =1,k
            obs(i,j) = zm(i,j)
            cor(i,j) = z(i,j)
            err(i,j) = delz(i,j)
3000  continue
      end
```

Listing of Computer File WCACM.FOR

```
c  this program was written for microsoft fortran 3.31, it should be
c  very similar to fortran 77.  the \ is not standard fortran, it
c  suppresses line feed on a prompt to the screen and may have to be
c  removed from format statements
c  the command pause may not be standard
c
c  activity coefficient model wcacm
c
      subroutine wcacm (z,zm,x,p,k,q,qv,l,n,m,mv,key,f,fz,fp,const)
      implicit real*8(a-h,o-z)
      integer q
      real*8 lngm1, lngm2
      real*8 z(q,k), zm(q,k), p(n), f(m,k), fz(m,q,k), fp(m,n,k),
     >       x(1,k), const(10)
c
c  z(1,k): mole fraction component 1
c  z(2,k): activity coefficient
c  const(1): v1, pure volume, component 1
c  const(2): kt1, pure isothermal compressibility, component 1
c  const(3): v2, pure volume, component 2
c  const(4): kt2, pure isothermal compressibility, component 2
c  const(5): t, temperature
c
      chi1 = const(1)/(const(2)*const(5)*83.13716)
      chi2 = const(3)/(const(4)*const(5)*83.13716)
      delchi = chi1 - chi2
      ak2 = p(2) * chi2 - p(1) * delchi
      u2 = p(1)
      v2 = chi2
      ak1 = p(1) * delchi - p(2) * chi2
      u1 = p(1) + p(2)
      v1 = chi1
      do 10 i = 1,k
         if(z(1,i) .gt. 1.0) z(1,i) = 1.0
         if(z(1,i) .lt. 0.0) z(1,i) = 0.0
         lngm1 = 1./ak1 * dlog(
     >           ((chi2 + delchi * z(1,i))/v1)**(1.+(chi2/delchi))*
     >           (u1/(p(1) + p(2) * z(1,i)))**(1.+(p(1)/p(2))))
         lngm2 = 1./ak2 * dlog(
     >             ((chi1 - delchi * (1.-z(1,i)))/v2)**(1.-(chi1/delchi))*
     >             (u2/(p(1) + p(2) - p(2) * (1.-z(1,i))))**(-p(1)/p(2)))
         f(2,i) = z(3,i) - lngm2
         f(1,i) = z(2,i) - lngm1
10    continue
      end
```

BIBLIOGRAPHY

Abramov, E. V., A. S. Mirzayain, and O. A. Devina, Izv. Akad. Nauk. Kaz. Ssr., Ser. Khim., 23, 29 (1973).

Absood, A. H., M. S. Tutunji, K. -Y. Hsu, and H. L. Clever, J. Chem. Eng. Data, 21, 304 (1976).

Anderson, T. F., D. S. Abrams and E. A. Grens II., AIChE J., 24, 20 (1978).

Andrews, A. W., and K. W. Morcom, J. Chem. Thermo., 3, 513 (1971).

Ansevin, A. T., D. E. Roark and D. A. Yphantis, Anal. Biochem., 34, 237 (1970).

Atoyan, V. A., and I. A. Mamedov, Russ. J. Phys. Chem., 50, 1772 (1976).

Beare, W. G., G. A. McVicar, and J. B. Fergusson, J. Phys. Chem., 34, 1310 (1930).

Becker, F., M. Kiefer, P. Rhensius, and H. D. Schaefer, Z. Phys. Chem. (Frankfurt), 92, 169 (1974).

Benson, M. S., and J. Winnick, J. Chem. Eng. Data, 4, 432 (1976).

Billes, F., and G. Y. Varsanyi, Acta. Chim. Acad. Sci. Hung., 35, 147 (1963).

Boelhouwer, J. W. M., Physica A, 26, 1021 (1960).

Boje, L., and A. Hvidt, J. Chem. Thermo., 3, 663 (1971).

Bridgmen, P. W., Proc. Am. Acad., 49, 3 (1913).

Britt, H. I., and R. H. Luecke, Technometrics, 15, 233 (1973).

Brown, I., and W. Fock, Aust. J. Chem., 10, 417 (1957).

Brown, I., and F. Smith, Aust. J. Chem., 7, 269 (1954).

Brown, I., and F. Smith, Aust. J. Chem., 8, 62 (1955).

Brown, I., and F. Smith, Aust. J. Chem., 10, 423 (1957).

Brown, N. M. D., J. F. Maguire and F. L. Swinton, J. Chem. Thermo, 10, 855 (1978).

Buck, E., Personal Communication to J. P. O'Connell (1978).

Burkat, R. K., and A. J. Richard, J. Chem. Thermo, 7, 271 (1975).

Cabannes, J., and Y. Rocard, La Diffusion Moleculaire de la Lumiere, Les Presses Universitaies de France, Paris, (1929).

Campanella, E. A., Ph.D. Dissertation, University of Florida (1984).

Campbell, A. N., and E. M. Kartzmark, J. Chem. Thermo., 5, 163 (1973).

Campbell, A. N., E. M. Kartzmark, and S. C. Anand, Can. J. Chem, 48, 1579 (1970).

Chen, C. -T., R. A. Fine, and F. J. Millero, J. Chem. Phys., 66, 2142 (1977).

Chevalier, J. L., and D. Bares, J. Chim. Phys. Phys. -Chim. Biol., 66, 1448 (1969).

Christian, S. D., E. Neparko and H. E. Affsprung, J. Phys. Chem., 64, 442 (1960).

Coumou, D. A., E. L. Mackor, and J. Hijmans, Trans. Faraday Soc., 50, 1539 (1964).

Coumou, D. J., and E. L. Mackor, Trans. Faraday Soc., 60, 1727 (1964).

Cullinan, H. T., Ind. Eng. Chem., Fundam., 7, 317 (1968).

Cullinan, H. T., and J. P. Lenczyk, Ind. Eng. Chem., Fundam., 8, 819 (1969).

Daubert, T. E., and R. P. Danner, Data Compilation Tables of Properties of Pure Compounds, Am. Inst. Chem. Eng., New York (1985).

Deming, W. E., Statistical Adjustment of Data, Wiley, New York, 1943.

Deshpande, D. D., and L. G. Bhatgadde, J. Phys. Chem., 72, 261 (1968).

Deshpande, D. D., and S. L. Oswal, J. Chem. Soc. Faraday Trans., 68, 1059 (1972).

Deshpande; D. D., and M. V. Pandya, Trans. Faraday Soc., 63, 2149 (1967).

Dezelic, G., Croat. Che. Acta., 45, 385 (1973).

Dolezalek, F., and F. Speidel, Z. Phys. Chem., 94, 72 (1920).

Doolittle, A. K., J. Chem. Eng. Data, 9, 275 (1964).

Dorfmuller, Th., G. Fytes, and W. Mersch, Ber. Bunsenges. Phys. Chem., 80, 389 (1976).

Dymond, J. H., N. Glen, J. Robertson, and J. D. Isdale, J. Chem. Thermo., 14, 1149 (1982).

Dymond, J. H., J. Robertson, and J. D. Isdale, Int. J. Thermophys., 2, 223 (1981).

Dyson, R. D., Anal. Biochem., 33, 193 (1970).

Easteal, A. J., and L. A. Woolf, J. Chem. Thermo., 17, 49 (1985).

Eastman, D., A. Hollinger, J. Kenemuth, and D. Rank, J. Chem. Phys., 50, 1567 (1969).

Eduljee, H. E., D. M. Newitt and K. E. Weale, J. Chem. Thermo., 11, 3086 (1951).

Einstein, A., Ann. Physik., 25, 205 (1908).

Ewing, M. B., B. J. Levien, K. N. Marsh, and R. H. Stokes, J. Chem. Thermo., 2, 689 (1970).

Ewing, M. B., and K. N. Marsh, J. Chem. Thermo., 9, 371 (1977).

Fishman, L., and R. D. Mountain, J. Phys. Chem., 74, 2178 (1970).

Fury, M., G. Munie, and J. Jonas, J. Chem. Phys., 70, 1260 (1979).

Garrett, P. R., J. M. Pollock and K. W. Morcom, J. Chem. Thermo., 5, 569 (1973).

Gibson, R. E., and O. H. Loeffler, J. Chem. Phys., 43, 207 (1939a).

Gibson, R. E., and O. H. Loeffler, J. Am. Chem. Soc., 61, 2515 (1939b).

Gibson, R. E., and O. H. Loeffler, J. Am. Chem. Soc., 63, 898 (1941).

Glanville, J. W., and B. H. Sage, Ind. Eng. Chem., 41, 1272 (1949).

Gmehling, J., U. Onken, W. Arlt, P. Grenzheuser, U. Weidlich and B. Kolbe, Volume 1, VLE Data Collection, DCEHEMA, Frankfurt (1977-1984).

Gouel, P., Bull. Cent. Rech. Explor.-Prod. Elf-Aquitaine, 2, 211 (1978).

Gropper, L., Anal. Biochem., 7, 401 (1964).

Guillen, M. D., and C. G. Losa, J. Chem. Thermo., 10, 567 (1978).

Gupta, A. C., and R. W. Hanks, Thermochim Acta, 21, 143 (1977).

Handa, Y. P., and G. C. Benson, Fluid Phase Equilibria, 3, 185 (1979).

Hanks, R. W., A. C. Gupta and C. K. H. Yee, Thermochim Acta, 23, 57 (1978).

Holman, J. P., Experimental Methods for Engineers, McGraw-Hill, New York (1971).

Holtzlander, G. W., and I. W. Riggle, AIChE J., 1, 312 (1955).

Hsu, H-W., Separations by Centrifugal Phenomena, Techniques of Chemistry, Volume XVI, E. S. Perry, ed., Wiley, New York (1981).

Huang, Y. H., Ph.D. Dissertation, University of Florida (1986).

Hwan, R., C. A. Miller, T. Fort, J. Coll. Int. Sci., 68, 221 (1979).

Isdale, J. D., J. H. Dymond, and T. A. Brawn, High Temp.-High Pressures, 11, 571 (1979).

Iwasaki, K., M. Tanaka, and T. Fujiyama, Bull. Chem. Soc. Japan, 49, 2719 (1976).

Johnson, J. S., K. A. Kraus and T. F. Young, J. Am. Chem. Soc., 76, 1436 (1954).

Johnson, J. S., G. Scatchard and K. A. Kraus, J. Phys. Chem., 63, 787 (1959).

Jonas, J., D. Hasha, and S. G. Huang, J. Phys. Chem., 84, 109 (1980).

Kalliorinne, K., Suom. Kemistilethi B, 42, 424 (1969).

Kashiwagi, H., T. Fukunaga, Y. Tanaka, H. Kubota, and T. Makita, Rev. Phys. Chem. Japan, 49, 70 (1979).

Kato, T., J. Phys. Chem., 88, 1248 (1984).

Kato, T., and T. Fujiyama, J. Phys. Chem., 80, 2771 (1976).

Kato, T., T. Fujiyama, and H. Nomura, Bull. Chem. Soc. Japan, 55, 3368 (1982).

Katz, M., P. W. Lobo, A. S. Minano, and H. Solimo, Can. J. Chem., 49, 2605 (1971).

Katz, M., P. W. Lobo and H. Solimo, An. Asoc. Quim. Argent., 61, 83 (1973).

Kireev, V. A., and I. P. Sitnikov, Zh. Fiz. Khim., 15, 492 (1941).

Kirkwood, J. G., and F. P. Buff, J. Chem. Phys., 19, 774 (1951).

Kirkwood, J. G., and R. J. Goldberg, J. Chem. Phys., 18, 54 (1950).

Kiyohara. O., and K. Arakawa, Bull. Chem. Soc. Japan, 43, 3037 (1970).

Kubota, H., S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka and T. Makita, Rev. Phys. Chem. Japan, 49, 59 (1979).

Kuis, A., Z. Physik. Chec. B., 34, 13 (1936).

Kumagai, A., and S. Takahashi, Chem. Lett., 7, 971 (1982).

Kumagai, A., and S. Takahashi, J. Chem. Thermo., 17, 977 (1985).

Kuss, E., and M. Taslimi, Chem-Ing.-Tech., 42, 1073 (1970).

Lamb. J. A., and A. F. Hunt, Chem. Eng. J., 14, 73 (1977).

Landau, L. D., and E. M. Liftshitz, Statistical Physics, Part 1, 3rd Edition, Pergamon Press, New York, (1980).

Litvinov, N. D., Zh. Fiz. Khim., 26, 1144 (1952).

Loblen, G., and J. M. Prausnitz, Ind. Eng. Chem., Fundam., 21, 109 (1982).

Loiseleur, H., J-. C. Merlin and R. A. Paris, J. Chim. Phys., 64, 634 (1967).

Machado, J. R. S., and W. B. Streett, J. Chem. Eng. Data, 28, 218 (1983).

Maguire, J. F., J. C. F. Michielsen and G. Rakhorst, J. Phys. Chem., 85, 2971 (1981).

Marsh, K. N., and C. Burfitt, J. Chem. Thermo., 7, 955 (1975).

Marsh, K. N., J. Chem. Thermo., 2, 359 (1970).

Mathias, P. M., Ph.D. Dissertation, University of Florida (1978).

Mathias, P. M., and J. P. O'Connell, Adv. Chem. Ser., 182, 97 (1979).

Mathias, P. M., and J. P. O'Connell, Chem. Eng. Sci., 36, 1123 (1981).

Matsuo, S., and A. VanHook, J. Chem. Phys., 88, 1032 (1984).

Mertl, I., Collect. Czech. Chem. Commun., 37, 366 (1972).

Mikhail, S. Z., and W. R. Kimel, J. Chem. Eng. Data, 6, 533 (1961).

Mikhail, S. Z., and W. R. Kimel, J. Chem. Eng. Data, 8, 323 (1963).

Miller, G. A., J. Phys. Chem., 71, 2305 (1967).

Miller, G. A., and C. S. Lee, J. Phys. Chem., 72, 4644, (1968).

Miller, G. A., and C. S. Lee, J. Phys. Chem., 77, 2441 (1973).

Miller, L. P., H. N. Wachter, and V. Fried, J. Chem. Eng. Data, 20, 417 (1975).

Mopsik, F. I., J. Chem. Phys., 50, 2559 (1969).

Nagai, J., and N. Isii, J. Soc. Chem. Ind. Japan, 38, 86 (1935).

Nagata, I., J. Chem. Eng. Data, 7, 461 (1962).

Newitt, D. M., and K. E. Weale, J. Chem. Soc., 3092 (1951).

Nichol, L. W., and D. J. Winzor, J. Phys. Chem., 80, 1980 (1976).

Nigam, R. K., B. S. Mahl and P. P. Singh, J. Chem. Thermo., 4, 41 (1972).

Niini, A., Ann. Acad. Sci. Fenn., A55, 2 (1940).

Ocon, J., G. Tojo and L. Espada, An. Quim., 65, 735 (1969).

Ornstein, L. S., and F. Zernike, Verslag Akad. Wetenschappen, 23, 582 (1914).

Oster G., Chem. Rev., 43, 319 (1948).

Ozawa, S., N. Ooyatsu, Y. Yamabe, S. Honmo, and Y. Ogino, J. Chem. Thermo., 12, 229 (1980).

O'Connell, J. P., Mol. Phys., 20, 27 (1971).

O'Connell, J. P., Fluid Phase Equilibra, 6, 21 (1981).

O'Connell, J. P., Proc. Second Int. Conf. FOCAPD, A. W. Westerberg and H. H. Chien, Eds., CACHE, Ann Arbor, MI, 219 (1983).

Palmer, D. A., and B. D. Smith, J. Chem. Eng. Data, 17, 71 (1972).

Parkhurst, Jr., H. J., and J. Jonas, J. Chem. Phys. 63, 2698 (1975a).

Parkhurst, Jr., H. J., and J. Jonas, J. Chem. Phys. 63, 2705 (1975b).

Pearce, P. J., and W. Strauss, Aust. J. Chem., 21, 1213 (1968).

Perry, R. H., and C. H. Chilton, Chemical Engineers' Handbook, 5th Edition, McGraw-Hill, New York (1973).

Ponc, M., and G. R. Ratcliff, Can. J. Chem. Eng., 54, 326 (1976).

Prausnitz, J. M., C. A. Eckert, R. V. Oyrc and J. P. O'Connell, Computer Calculations for Multicomponent Vapor-Liquid Equilibria, Prentice-Hall, Englewood Cliffs (1967).

Rabinovich, I. B., and P. N. Nikolaev, Zh. Fiz. Khim., 34, 2289 (1960).

Ratcliff, G. A., and K. C. Chao, Can. J. Chem. Eng., 47, 148 (1969).

Ratzsch, M., and R. Findeisen, Z. Phys. Chem. (Leipzig), 261, 935 (1980).

Rau, G. P., Ph.D. Dissertation, State University of New York at Buffalo (1975).

Reamer, H. H., and B. H. Sage, Chem. Eng. Data Ser., 2, 9 (1957).

Rees, A. W., E. A. Lewis and M. S. DeBuysere, Anal. Biochem., 62, 19 (1974).

Renon, H., and J. M. Prausnitz, AIChE J., 14, 135 (1968).

Richard, A. J., J. Chem. Phys., 72, 4063 (1980).

Richard, A. J., K. T. McCrickard, and P. B. Fleming, J. Chem. Thermo., 11, 93 (1979).

Richards, E. G., and H. K. Schachman, J. Phys. Chem., 63, 1578 (1959).

Richards, E. G., D. Teller and H. K. Schachman, Anal. Biochem., 41, 189 (1971a).

Richards, E. G., D. Teller and H. K. Schachman, Anal. Biochem., 41, 215 (1971b).

Sahli, B. P., H. Gager, and A. J. Richard, J. Chem. Thermo, 8, 179 (1976).

Schornack. L. G., and C. A. Eckert, J. Phys. Chem., 74, 3014 (1970).

Schreiber, L. B., and C. A. Eckert, Ind. Eng. Chem. Process Des. Dev., 10, 572 (1971).

Schroeder, J., V. H. Schiemann, and J. Jonas, J. Chem. Phys., 69, 5479 (1978).

Schroeder, J., V. H. Schiemann, P. T. Sharko, and J. Jonas, J. Chem. Phys., 66, 3215 (1977).

Seitz, W. and G. Lechner, Ann. Phys. (Leipzig), 49, 93 (1916).

Sethy, A., and H. T. Cullinan, AIChE J., 18, 829 (1972).

Sieg, L., J. L. Cruetzen, and W. Jost, Z. Phys. Chem., 198, 263 (1951).

Srinivasan, K. R., and R. L. Kay, J. Sol. Chem., 6, 357 (1977).

Takagi, T., Rev. Phys. Chem. Japan, 48, 17 (1978).

Takagi, T. and H. Teranishi, J. Chem. Thermo., 14, 1167 (1982a).

Takagi, T., and H. Teranishi, J. Chem. Thermo., 14, 577 (1982b).

Tanaka, Y., T. Yamamoto, Y. Satomi, H. Kubota and T. Makita, Rev. Phys. Chem. Japan, 47, 12 (1977).

Tasic, A., B. Djordjevic, and D. Grozdanic, Chem. Eng. Sci., 33, 189 (1978).

Tekac, V., I. Cibulka and R. Holub, Fluid Phase Equilibria, 19, 33 (1985).

Treszczanowicz, A. J., and G. C. Benson, J. Chem. Thermo., 9, 1189 (1977).

Ucovenko, V. V., and T. F. Mazanko, Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhngl., 15, 1654 (1972).

Van Ness, H. C., and M. M. Abbott, Classical Thermodynamics of Non Electrolyte Solutions, McGraw-Hill, New York (1982).

Varma, K. T. R., M. K. Kumaran, and T. S. Seetharaman, J. Chem. Thermo. 8, 657 (1976).

Werner, G., and H. Schuberth, J. Prakt. Chem., 31, 225 (1966).

Wichterle, I., J. Linek and E. Hala, Vapor-Liquid Equilibrium Data Bibliography, Elsevier, Amsterdam (1973).

Williams, Jr., R. C., Anal. Biochem., 48, 164 (1972).

Williams, Jr., R. C., Methods Enzymol., 48F, 185 (1978).

Williams, Jr., R. C., Personal Communication (1985).

Wilson, G. M., J. Am. Chem. Soc., 86, 127 (1964).

Winnick, J., and J. Kong, Ind. Eng. Chem. Fundam., 13, 292 (1974).

Winnick, J., and J. E. Powers, AIChE J., 3, 460, (1966).

Wistozki, K. D., and A. Wurflinger, J. Phys. Chem. Solid, 43, 13 (1982).

Wolff, H., and H. E. Hoeppel, Ber. Bunsenges. Phys. Chem., 72, 1173 (1968).

Zawidzki, V. J., Z. Phys. Chem., 35, 129 (1900).

BIOGRAPHICAL SKETCH

Robert Joseph Wooley was born in Pontiac, Michigan, on September 2, 1954. He graduated from The University of Michigan, in May of 1976 with a Bachelor of Science in Engineering degree in chemical engineering. After working for two and one-half years for Dow Chemical Company in Midland, Michigan in their Process Development Department he returned to The University of Michigan. There, working with Dr. Joseph J. Martin developing a new equation of state for steam, he received a Master of Science in Engineering degree in chemical engineering in August of 1979. He then worked in Process Engineering and Research for Dow Corning, Midland, Michigan, and Carrollton, Kentucky, for nearly five years. He then decided to attend the University of Florida to begin studies toward a Doctor of Philosophy degree in chemical engineering. He is a member of AIChE and ACS and is a registered professional engineer in the states of Florida and Michigan.

I certify that I have read this study and that in my opinon it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John P. O'Connell

John P. O'Connell, Chairman
Professor of Chemical Engineering

I certify that I have read this study and that in my opinon it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles E. Reid

Charles E. Reid
Professor of Chemistry

I certify that I have read this study and that in my opinon it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Timothy J. Anderson

Timothy J. Anderson
Associate Professor of Chemical Engineering

I certify that I have read this study and that in my opinon it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dale Kirmse

Dale Kirmse
Associate Professor of Chemical Engineering

I certify that I have read this study and that in my opinon it conforms to the acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gerald Westerman-Clark

Gerald Westerman-Clark
Associate Professor of Chemical Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1987

Herbert A. Bevis

Dean, College of Engineering

Dean, Graduate School

UNIVERSITY OF FLORIDA
3 1262 08554 0275